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HYDRATES OF THE METHANE-CARBON DIOXIDE-
HYDROGEN SULFIDE SYSTEM

by

JAMES MICHAEL HUTTON

A THESIS

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled HYDRATES OF THE METHANE-CARBON DIOXIDE-HYDROGEN SULFIDE SYSTEM submitted by James Michael Hutton in partial fulfilment of the requirements for the degree of Master of Science.

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ABSTRACT

Hydrate equilibria data are presented for four vapor mixtures of methane, carbon dioxide, hydrogen sulfide in the three phase region of hydrate, water-rich liquid and vapor.

The formation of hydrates from vapor and aqueous liquid in a quaternary system is dependent on pressure temperature and two composition variables and therefore cannot be represented graphically in two dimensions. A means is presented to predict initial hydrate forming conditions in systems of methane concentration in the vapor phase from 65 to 100 percent with no restriction placed on the ratio of carbon dioxide to hydrogen sulfide.

Equilibrium ratios were used to calculate initial hydrate forming conditions for the system under study but the results were found to deviate considerably from experimental data. Suggestions are made to account for this behavior.

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NOMENCLATURE

n	number of moles
F	number of degrees of freedom
C	number of components
P	pressure; in phase rule - no. of phases
T	temperature
V	vapor
I	ice
L ₂	hydrocarbon-rich liquid
L ₁	water-rich liquid
H	hydrate
K _{vs}	equilibrium ratio (solid vapor)
y	mole fraction of component in vapor phase
z	mole fraction of component in the solid phase (water free basis)

I. INTRODUCTION

Many gases under pressure and in the presence of free water will form white crystalline solids known as gas hydrates. The formation of these materials may be represented by the reversible reaction



This is a univariant equilibrium in that at a given temperature the pressure of the gas has a single value.

X-ray diffraction studies have shown that gas hydrates crystallize in either of two molecular structures referred to as Structures I and II. Both of these are ice-like tetrahedral structures taking the form of a modified body centered cubic lattice. At each corner and in the center of the lattice is found a pentagonal dodecahedral array of water molecules which form approximately spherical cavities in which hydrating gas molecules may be situated. This arrangement of water molecules is referred to as the host lattice and is a metastable form completely stabilized only when hydrating gas molecules enter the cavities. Hydrogen bonding exists between the individual water molecules and van der Waals' forces exist between the solute gas and the water molecules. Gas hydrates thus belong to the family of inclusion compounds generally known as clathrates.

Structures I and II differ in the size of the cavities and the orientation of the water molecules in space. It follows that Structure II will form only when the molecules of the hydrating gas are too large to be accommodated in the cavities of Structure I. Although it is not completely understood why some gases form hydrates and why others do not, it is generally accepted that the following conditions must be met:

1. The solute gas molecules must show no specific chemical interaction with the water molecules forming the host lattice. For example, neither hydrochloric acid nor ammonia form hydrates.

2. The solute gas molecules must be small enough to fit into the cavities of Structures I or II. Hydrocarbons in the homologous series above normal butane are not known to form hydrates.

3. The solute gas must be polarizable to the extent that it will stabilize the host lattice. Helium, neon and hydrogen are not known to form hydrates by themselves but they do add to the stability of a hydrate of a more polarizable solute simultaneously present.

Phase equilibria of hydrate-forming systems are usually represented with a pressure temperature diagram. For the system of one hydrate forming gas in the presence of water there exists a locus of equilibrium temperatures and pressures for which three phases coexist as shown by Figure 1. The line AB represents three phase equilibria, hydrate, water-rich

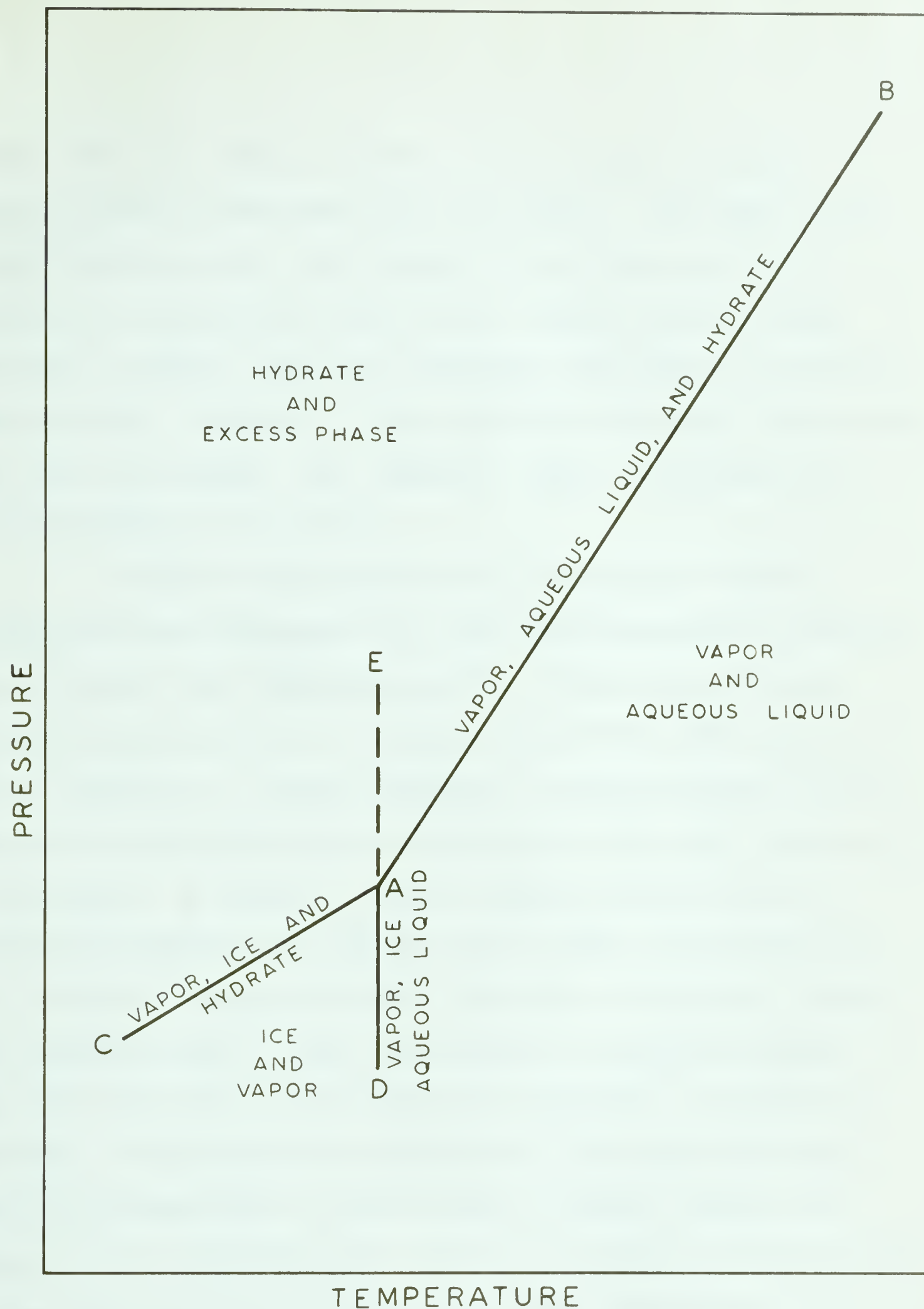


FIG.1 HYDRATE EQUILIBRIA FOR THE BINARY, SOLUTE GAS WATER SYSTEM WHERE THE SOLUTE GAS HYDRATE ABOVE ITS CRITICAL TEMPERATURE

liquid and vapor (HL_1V). This is the locus of initial hydrate forming conditions for the system. The water-rich liquid freezing point line shown in the figure as AD is essentially vertical at 32°F if the solubility of the gas in water is small. Line AC represents equilibria of hydrate, vapor and ice. Point A is the quadruple point for the system when the four phases, ice, hydrate, vapor, and water-rich liquid, ($IHVL_1$) are present.

In this investigation initial hydrate forming conditions were determined for four vapor mixtures of methane, carbon dioxide and hydrogen sulfide. Many gas producing reservoirs particularly in Alberta have these three gases as major components. Ternary systems of methane-carbon dioxide-water and methane-hydrogen sulfide-water have been previously investigated. A further study of hydrate equilibria for systems containing these three solute gases is warranted in view of the extremely non-ideal behavior of hydrogen sulfide and carbon dioxide. Also, the ability to predict hydrate equilibria for this system would be desirable. A graphical technique to represent the quaternary system was developed permitting prediction of three phase, hydrate, water-rich liquid, vapor equilibria for systems of methane concentrations in the range from 65 to 100 percent. No restriction was placed on the carbon dioxide to hydrogen sulfide ratio.

II. LITERATURE SURVEY

A. History

The first observation of hydrate formation was made in 1810 by Humphrey Davy(5) while cooling a saturated solution of chlorine and water below 9°C. In 1840 Woelher(5) reported a hydrate of hydrogen sulfide and in 1878 an acetylene hydrate was discovered by Cailletet(5). Carbon dioxide was observed to form a hydrate by Wroblewsky(5) in 1882. The initial work on investigation of conditions for hydrate formation was done by Villard(23) working with methane, ethane, ethylene and acetylene. Villard's work is regarded as the first reliable investigation into initial hydrate forming conditions. However, in his work Villard observed a maximum temperature for a hydrate to exist for ethane, ethylene and acetylene and suspected that such a maximum should exist for methane. Limited by his apparatus, he could only postulate a temperature of 70.7°F but could not verify it experimentally. Subsequently it has been shown that no such maximum exists.

Between 1880 and 1900 Schutzenberger(5) observed the first mixed hydrate. This type of hydrate is formed from two or more solute gases in the vapor phase. He postulated that the mixed hydrate is one compound having a unique melting point at each pressure. This implied that mixed hydrates are not two single hydrates but one in which all the components are associated. Mixtures of carbon disulfide

and hydrogen sulfide were studied in this investigation.

In the same period, interest developed in the determination of the hydrate composition. Since hydrates form in pressured systems they cannot easily be sampled for analysis. As crystallization occurs occlusion of water in the crystals becomes inevitable and an accurate determination of the amount of water becomes impossible. De Forcrand(4) presented a thermodynamic method for determining the hydrate composition which was subsequently improved upon by Roberts et al(16). An excellent review of methods for determining hydrate compositions is presented by Parent(14).

Following this work in the later 1800's the phenomena of hydrate formation became little more than a scientific curiosity. In 1934 industrial interest was stimulated by E.G. Hammerschmidt(5) who reported that "freezing" in gas transmission lines was due to hydrate formation. It was also noted that low spots, elbows and valves were places where hydrates could be initiated due to the presence of free water. In this work Hammerschmidt investigated initial hydrate forming conditions for various natural gases and realized that hydrate formation was dependent on pressure, temperature and vapor phase composition.

Further experimental work was continued by the U.S. Bureau of Mines with Deaton and Frost(2,3) investigating initial hydrate forming conditions for methane, propane and and three natural gases. A secondary objective of this work

was to determine means of preventing hydrate formation. Glycols, alcohols and other hygroscopic materials were found to render water unavailable for hydration.

In 1942 Carson and Katz(1) studied the methane-propane system. This work involved a study of the four phase region, hydrate, water-rich liquid, hydrocarbon-rich liquid and vapor. Conditions for these four phases to coexist in equilibrium were observed to follow a single curve on a pressure-temperature diagram. This information was found to be compatible with the phase rule and was considered to be verification of the hydrate being one isomorphous phase. Further observations indicated a trend to increasing gas gravity as the hydrate was decomposed. This behavior is typical of solid solutions.

Wilcox, Carson and Katz(25) suggested that a solid-vapor equilibrium ratio, similar to that used in vapor-liquid equilibria, is applicable for the prediction of initial hydrate forming conditions.

The solid vapor equilibrium ratio is defined by the following equation:

$$K_{svi} = \frac{y_i}{z_i}$$

where K_{svi} = solid vapor equilibrium ratio for component i
 y_i = mole fraction of component i in the vapor phase (on a water free basis)
 z_i = mole fraction of component i in the solid phase (on a water free basis)

With available data equilibrium ratios were calculated for methane. The logarithms of the equilibrium ratios versus temperature were plotted with pressure as the parameter. Initial hydrate forming conditions were then observed for gaseous mixtures of methane and one other component.

Since

$$\sum_{i=1} z_i = 1.0$$

and rearranging

$$\sum_{i=1} \frac{Y_i}{K_{svi}} = 1.0$$

Knowing the equilibrium ratio for methane, the equilibrium ratio for any other component may be calculated. With knowledge of the equilibrium ratios for several pure gases the initial hydrate forming conditions for mixtures of known composition can be predicted by trial and error. Such a calculation is presented in the appendix.

B. Previous Work on the System Under Investigation

1. The Methane-Water System

Villard(23) in 1888 published the first reliable data on the methane-water system. In 1940 Roberts et al(16) published more complete pressure-temperature diagrams for the

methane-water and ethane-water systems. Data are presented for ice, hydrate, vapor (IHV) equilibria and water-rich liquid, hydrate and vapor equilibria (L_1HV). An improvement to de Forcrand's thermodynamic method for the determination of hydrate composition is also given. Kobayashi and Katz(11) studied the methane-water system with pressures varying from 4900 lbs/in² to 11,200 lbs/in² and temperatures varying from 72.5°F to 83.9°F, respectively. This work disproves Villard's postulate that the maximum temperature for the methane hydrate to exist is 70.7°F.

2. The Methane-Carbon Dioxide-Water System

Unruh and Katz(22) have studied the carbon dioxide-water binary system and the methane-carbon dioxide-water ternary system. They report a quadruple point for the carbon dioxide-water system of 653 lbs/in² and 49.8°F. Using the method developed by Wilcox, Carson and Katz, equilibrium ratios have been determined for carbon dioxide.

3. The Hydrogen Sulfide-Water System

The phase behavior of the hydrogen sulfide-water system has been studied by Selleck, Carmichael and Sage(20). Data are presented on the three phase, hydrate, vapor and water-rich liquid (HL_1V) locus. The quadruple point is reported as 327.4 lbs/in² abs. and 85.1°F. Pressure-composition phase diagrams are also presented in this work.

4. The Methane-Hydrogen Sulfide-Water System

Noaker and Katz(13) have studied hydration conditions for mixtures of methane and hydrogen sulfide. Equilibrium ratios have been determined for hydrogen sulfide by the same method as that used for carbon dioxide.

III. THEORY

A. Application of the Phase Rule to Hydrate Forming Systems(17)

The phase rule in its simplest form may be written as follows:

$$F = C - P + 2$$

The total number of independent variables or the total number of conditions that may be arbitrarily imposed upon a closed system of C components and P phases is denoted by F , the number of degrees of freedom. If the number of components and the number of phases is such that the system may exist at only one temperature and one associated equilibrium pressure, it is said to be invariant and consequently has no degrees of freedom. The triple point of water exemplifies such a condition. When there is one degree of freedom one variable must be arbitrarily fixed in order to completely define the system. For example, with a single component existing in two phases, the temperature (or the pressure) alone is sufficient to define the system and a locus of conditions of temperatures and pressures may be plotted, commonly known as the vapor pressure curve. With two degrees of freedom a surface is generated while with three degrees of freedom the system may be represented by a volume. A gas hydrate is truly one solid isomorphous phase and the following hydrate forming systems will serve to illustrate the applicability of the phase rule.

B. Binary Systems

For systems of one solute gas and water, there exists a locus of conditions of temperature and associated equilibrium pressures for which three phases, hydrate, water-rich liquid and vapor, (HL_1V) can exist. Figure 1 illustrates the phase behavior of a system in which the solute gas is hydrating above its critical temperature. The phase rule can readily be seen to apply, for two components exist in three phases along any line indicating one degree of freedom. Methane and nitrogen are examples of gases which portray this behavior.

Figure 2 represents a system where the solute gas hydrates below its critical temperature. The line JBF is the vapor pressure curve for the solute gas displaced slightly due to the presence of water. As the temperature and pressure are increased along the hydrate, water-rich liquid, vapor (HL_1V) curve, a point is reached at the intersection with the vapor pressure curve where a fourth phase occurs, viz. a liquid, rich in the solute component. The appearance of a fourth phase fixes the system to one single equilibrium temperature and pressure. This behavior is predicted by the phase rule for two components in four phases. The line BG, which is almost vertical, represents the solute-rich liquid, water-rich liquid, hydrate equilibria. This is the maximum temperature that Villard observed for the hydrate to exist. Carbon dioxide and hydrogen sulfide exemplify this type of behavior.

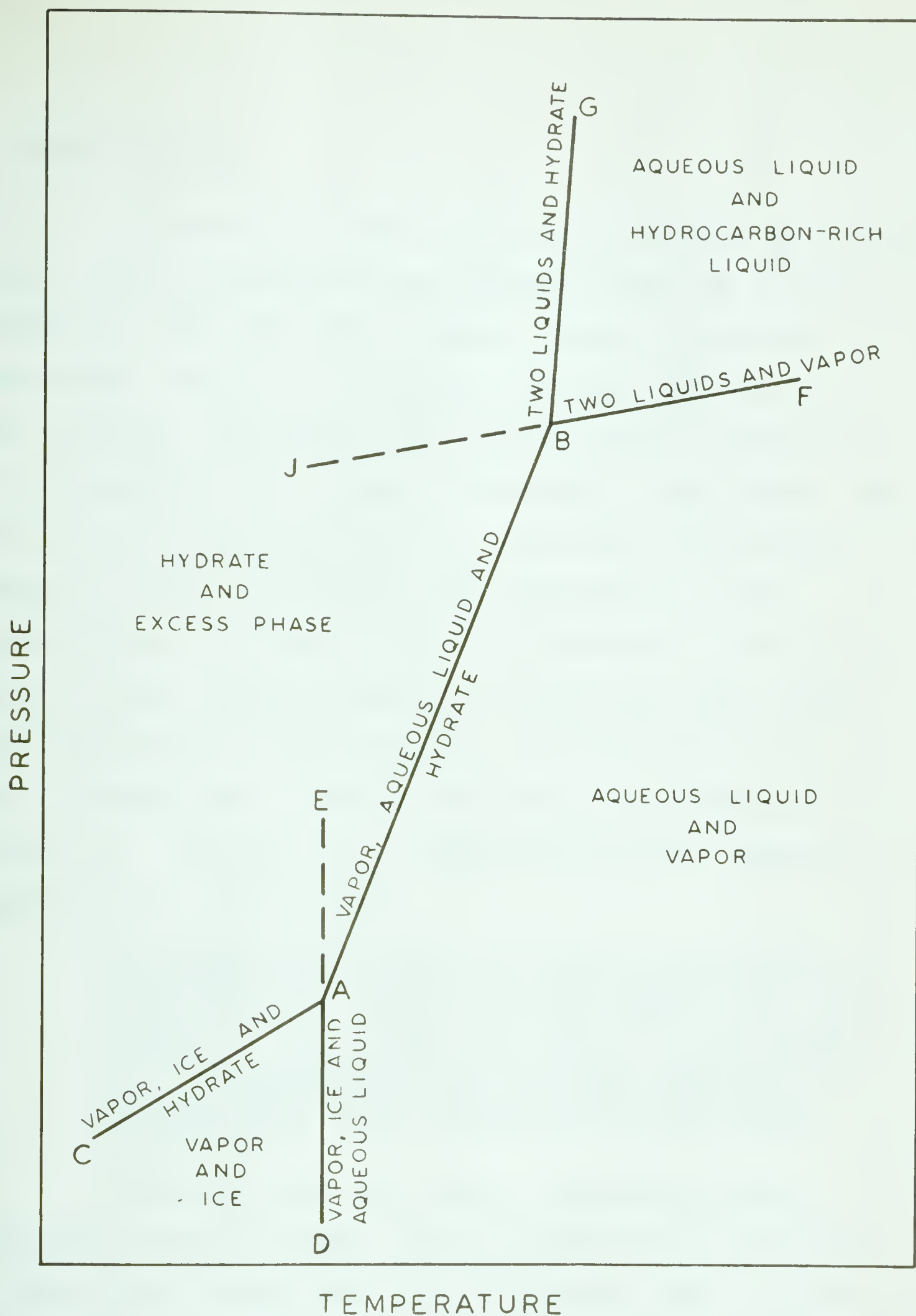


FIG.2 HYDRATE EQUILIBRIA FOR THE BINARY, SOLUTE GAS WATER SYSTEM WHERE THE SOLUTE GAS HYDRATE BELOW ITS CRITICAL TEMPERATURE

C. Ternary Systems

Consider the ternary system of two solute gases and water. One of the solute gases hydrates above its critical temperature, while the other hydrates below its critical temperature. Figure 3 illustrates the phase behavior of such a system. From phase rule considerations, the addition of one component adds a degree of freedom to the system. The lines AB and DE represent hydrate equilibria for the pure component solutes. The three phase equilibria is now represented by a surface and the lines between AB and DE are initial hydrate forming conditions for mixtures with vapor phase composition as the parameter. The curve BC is the locus of conditions for which four phases may coexist in equilibrium. Otto(15) in an investigation of the methane-propylene-water system states.

"The highest point where four phases would exist in equilibrium was found to be 1370 lb/in² abs. and 69.3°F when the system was approximately 34.8 mole% propylene on a water free basis. At this point critical phenomena were encountered and the vapor and hydrocarbon rich liquid phases appeared to form one phase thus terminating the four phase equilibrium."

Essentially the four phase, water-rich liquid, solute-rich liquid, hydrate, vapor (L_1L_2HV) locus terminates the three phase, water-rich liquid, hydrate, vapor, (L_1HV) surface. Furthermore, the four phase (L_1L_2HV) locus is itself terminated by the occurrence of critical phenomena.

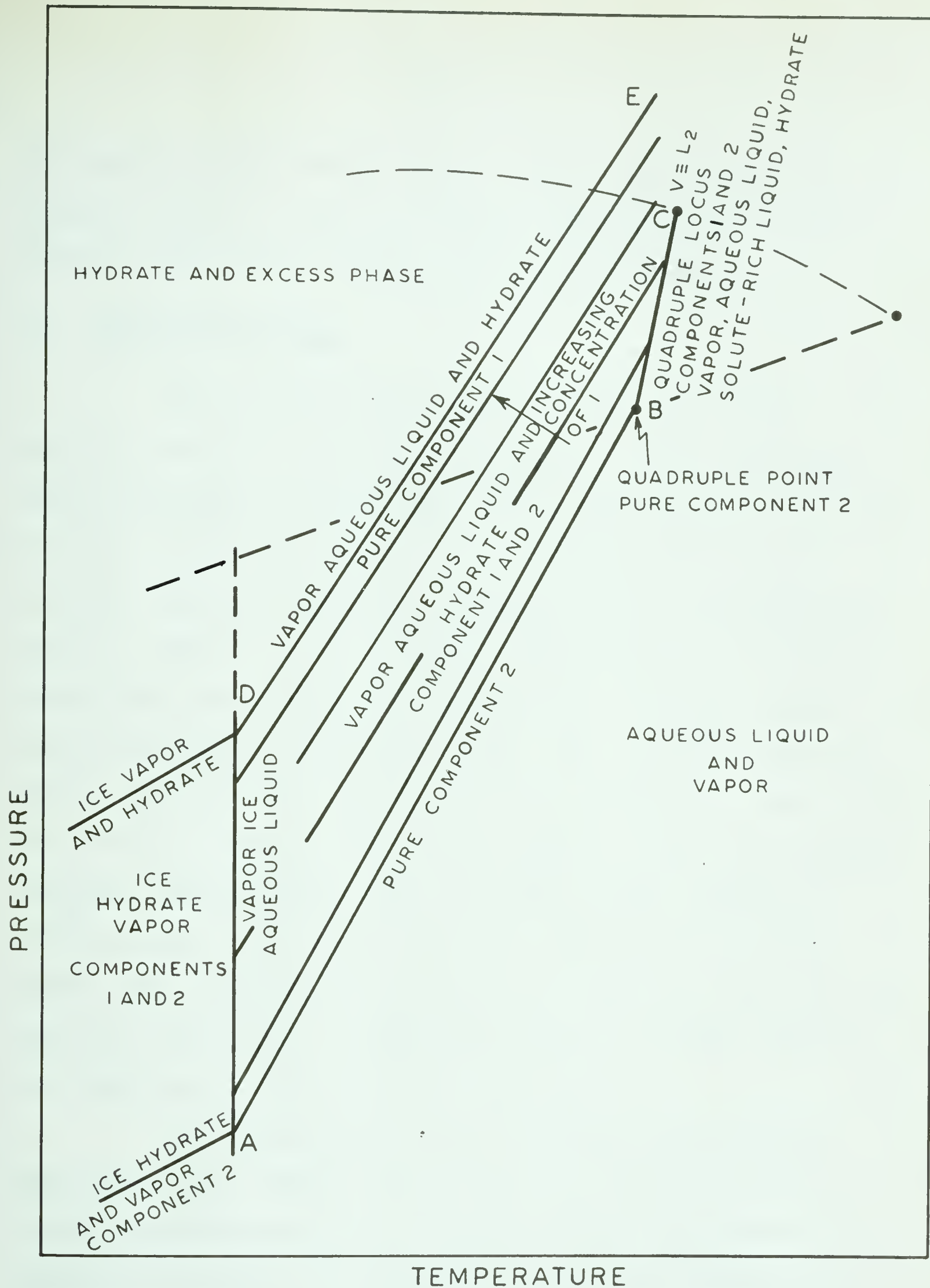


FIG.3 HYDRATE EQUILIBRIA FOR A TERNARY SYSTEM WHERE ONE SOLUTE GAS HYDRATES ABOVE ITS CRITICAL TEMPERATURE AND THE OTHER HYDRATES BELOW ITS CRITICAL TEMPERATURE

The methane-carbon dioxide-water system illustrates this behavior where in terms of Figure 3 methane would be component 1 and carbon dioxide would be component 2.

D. Quaternary Systems

The further addition of a solute gas, which hydrates below its critical temperature, to the previously described ternary system will add one more degree of freedom. Surfaces, lines and points in the ternary system become volumes, surfaces and lines, respectively in the quaternary system. Figure 4 is a schematic representation of hydrate equilibria for a quaternary system such as methane-carbon dioxide-hydrogen sulfide and water. The curves PA, DB and EC are vapor pressure curves with the points A, B, and C being the critical points for methane, carbon dioxide and hydrogen sulfide, respectively. The individual binary systems of methane water, carbon dioxide-water and hydrogen sulfide water three phase HL_1V equilibria are shown by curves JK, GD and FE, respectively. Quadruple points for carbon dioxide and hydrogen sulfide are given by D and E.

For quaternary systems the phase rule predicts that three phase (HL_1V) hydrate equilibria will generate a volume and that four phase (HL_1L_2V) hydrate equilibria will generate a surface. By considering the three possible ternary systems the boundaries of the four phase surface may be determined. The line DM is the four phase (HL_1L_2V) locus for



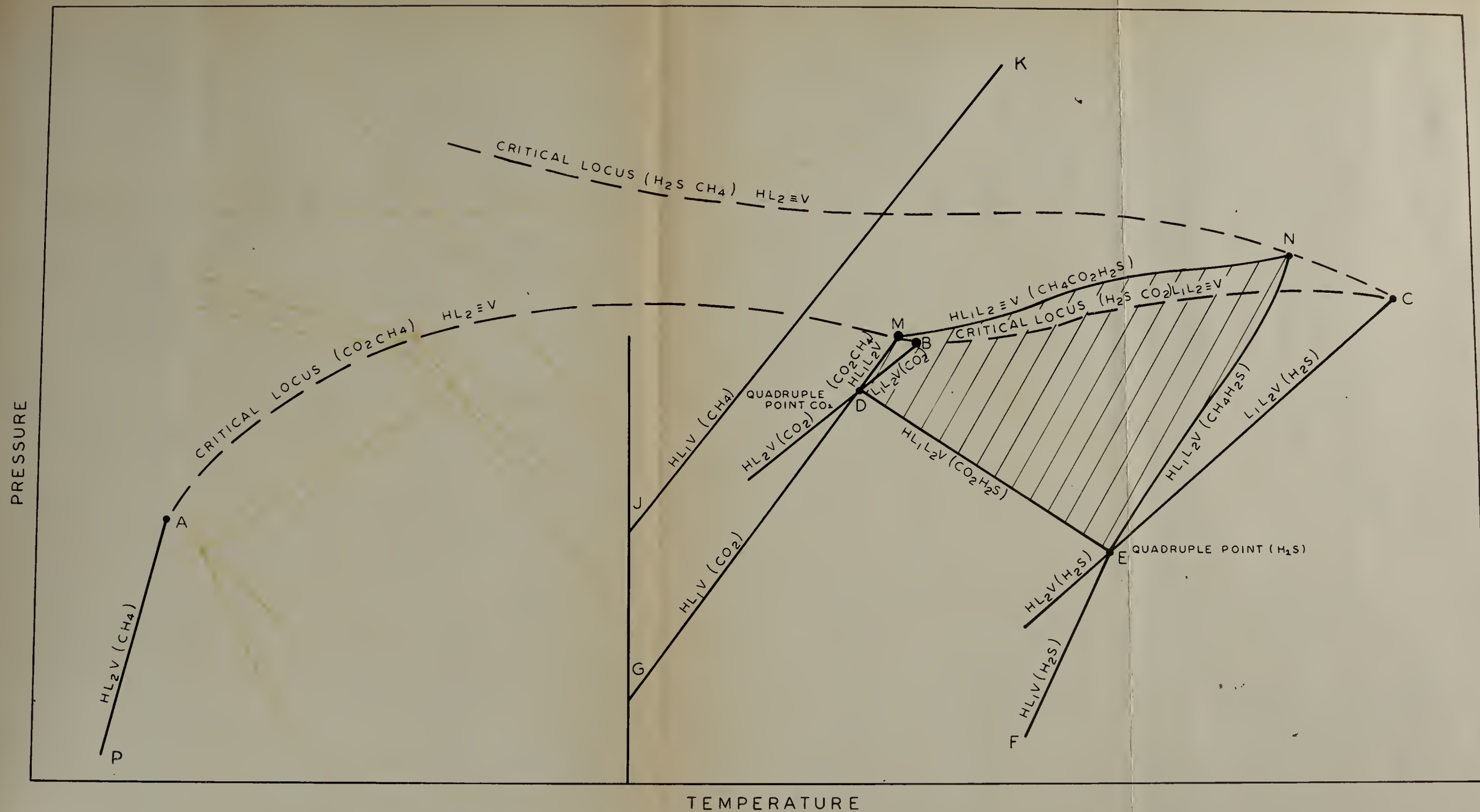


FIG. 4 HYDRATE EQUILIBRIA FOR THE QUATERNARY SYSTEM WHERE ONE COMPONENT HYDRATES ABOVE ITS CRITICAL TEMPERATURE AND THE OTHER TWO HYDRATE BELOW THEIR RESPECTIVE CRITICAL TEMPERATURES EG. CH₄-CO₂-H₂S SYSTEM

ternary systems of methane carbon dioxide and water. This curve is one boundary of the four phase surface for the quaternary system. Similarly, the line EN is the four phase (HL_1L_2V) locus for the ternary system of methane hydrogen sulfide and water. It should be noted that both these curves are terminated at M and N by the occurrence of critical phenomena as described previously in the discussion of ternary systems.

A third boundary for the four phase surface is given by the four phase locus DE for the carbon dioxide-hydrogen sulfide-water system. In order to completely define the surface of four phase equilibria a curve is formed by the intersection of the four phase surface with the critical surface. This final boundary is terminated by points M and N.

Throughout this discussion the effect of water on the critical points, loci and vapor pressure curves for the solute gases was assumed to be negligible.

IV. EXPERIMENTAL

A. Experimental Apparatus

The equipment used in this investigation was similar to that used by previous workers(7,15,21). Basically the apparatus consists of three major parts:

1. an equilibrium cell mounted on trunions, encased in a lucite jacket and equipped with a thermocouple;
2. a mercury displacement pump for pressure control and injection of water;
3. a bath in which varsol is the temperature controlling fluid circulating through the lucite jacket surrounding the equilibrium cell.

Figure 8 is a schematic diagram showing the assembly of the apparatus.

1. The Equilibrium Cell

An equilibrium cell similar in appearance to a Jerguson liquid level gauge was constructed in the Chemical Engineering Shop. Specifications required that the cell withstand 5000 lbs/in^2 and that no reinforcement at the middle be present. The advantage to be gained by using such a cell would be to allow the sampling of any liquid phase through a moveable probe traversing the entire length of the cell.

The equilibrium cell, being symmetrical about its vertical axis may be considered as a uniformly loaded beam fixed at both ends as shown in Figure 5a. For such a system the following equations apply:

$$M = \frac{wlx}{2} - \frac{wx^2}{2} - \frac{wl^2}{12}$$

$$f = - \frac{Mc}{I}$$

where

M = bending moment, in. lbs.

x = distance along the beam, in.

l = length of the beam, in.

w = load, lbs/in.

f = fiber stress perpendicular to the beam
cross section, lbs/in²

c = distance from the area center of gravity of
the cross section, in.

I = moment of inertia about the area center of
gravity of the cross section, in.⁴

a. Calculation of the area center of gravity (cross-section over a bolt hole), Figure 5b.

$$0.734 \left(x - \frac{1}{4}\right) + 1 \frac{15}{32} \frac{\left(x - 1 \frac{1}{8}\right)^2}{2} = \frac{1 \frac{15}{32} \left(1 \frac{13}{16} - x\right)^2}{2}$$

$$x = 0.955 \text{ inches}$$

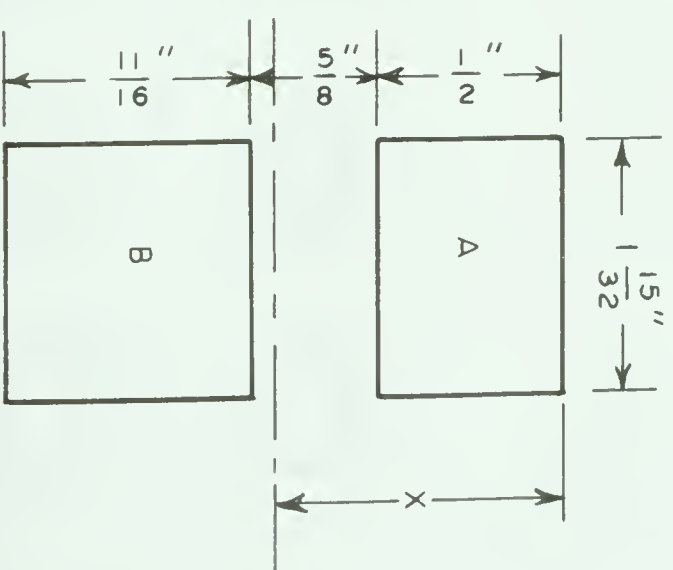
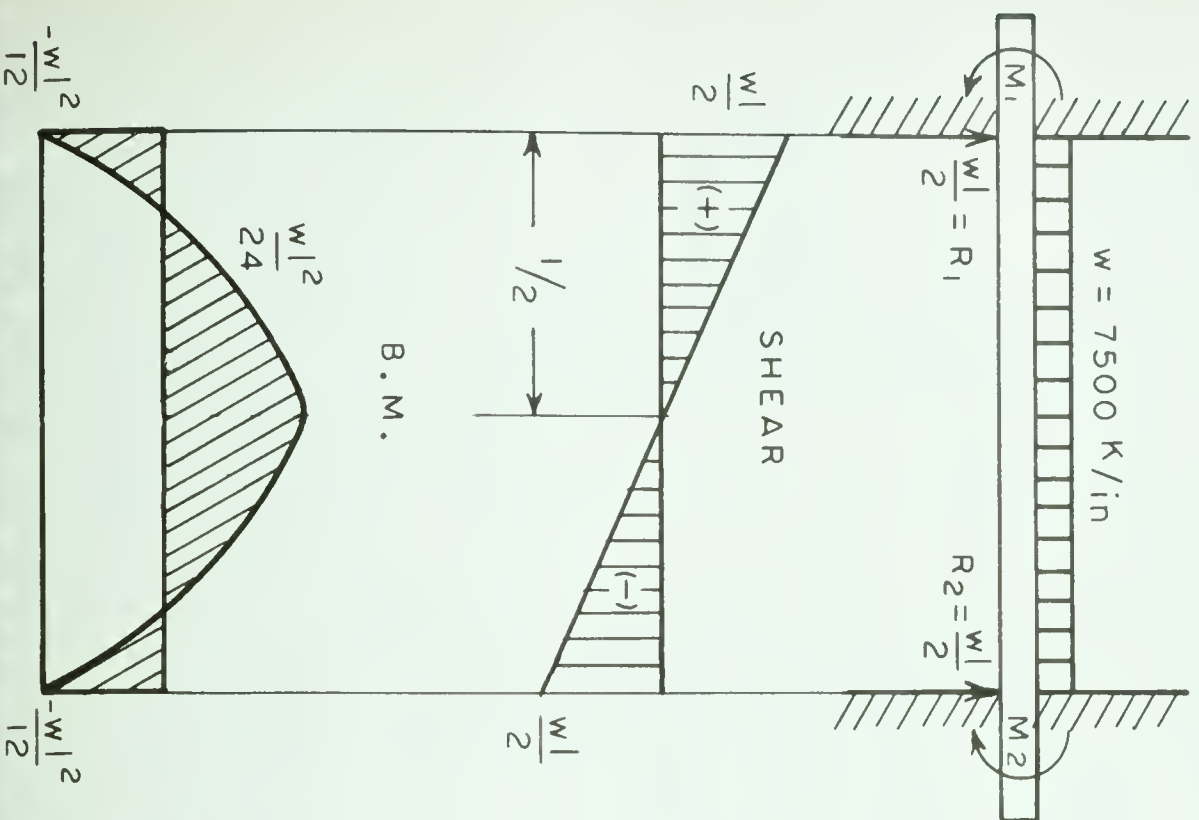
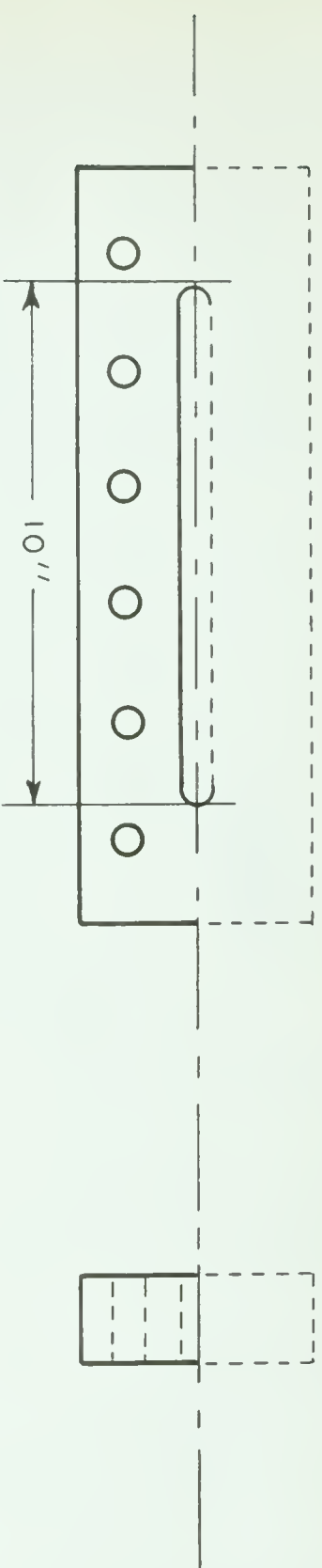


FIG. 5b CROSS SECTION OF
UNIFORMLY LOADED
BEAM OVER A BOLT HOLE

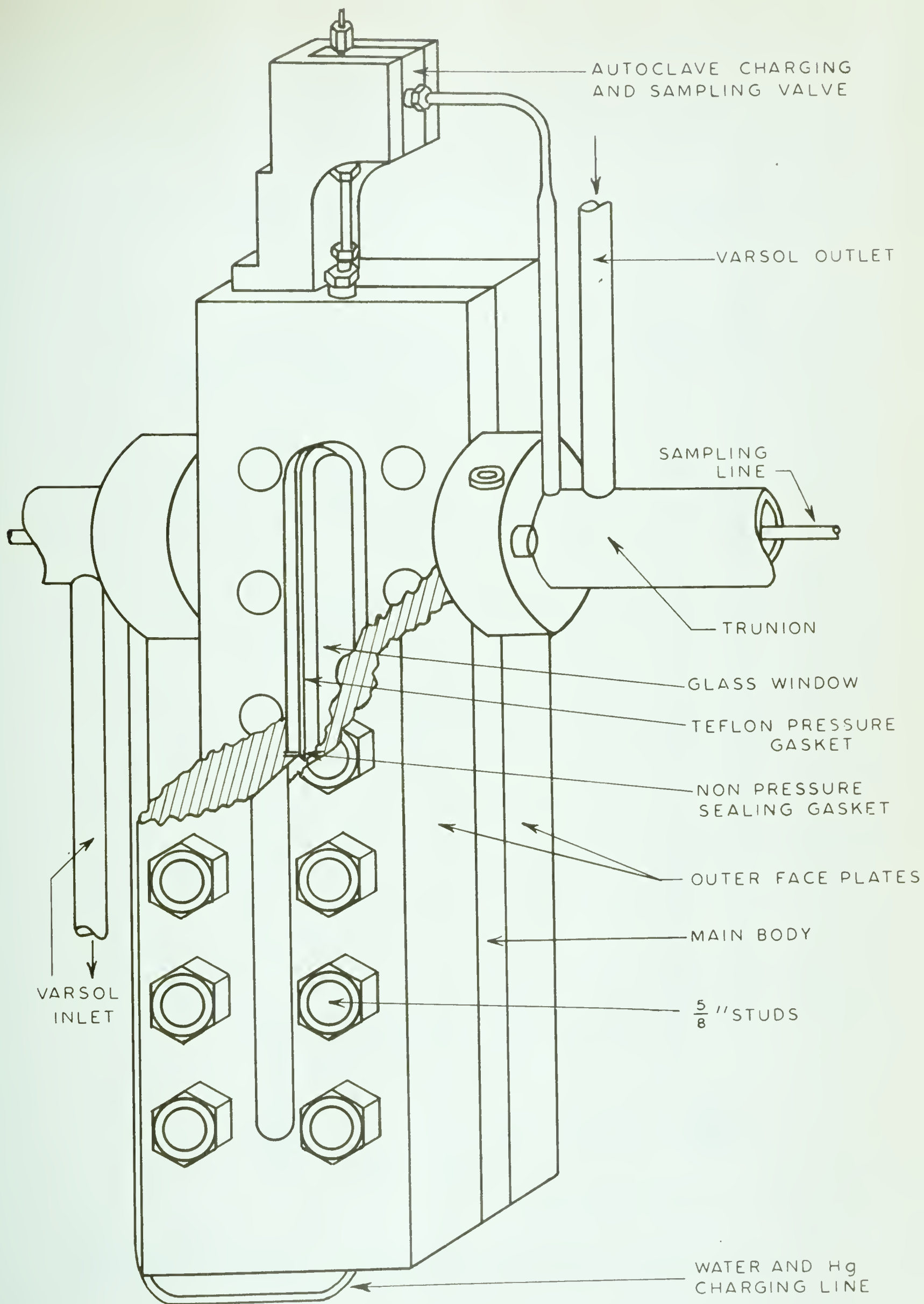
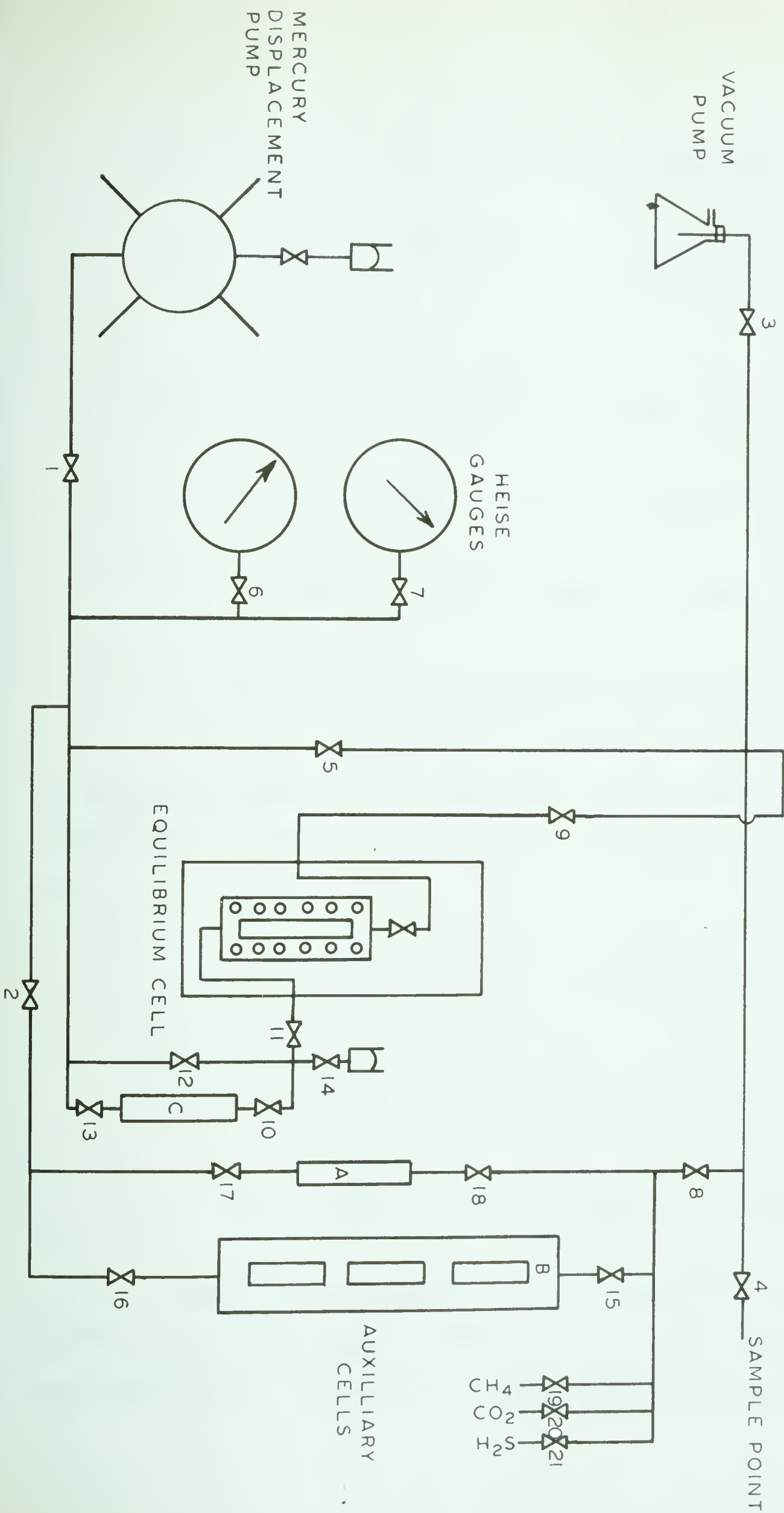


FIG.6 SCHEMATIC ASSEMBLY DRAWING OF EQUILIBRIUM CELL



b. Calculation of area moment of inertia, Figure 5b

$$I_A = \frac{bh^3}{12} = \frac{1 \frac{15}{32} \left(\frac{1}{2}\right)^3}{12} = 0.01525 \text{ in}^4$$

$$I_B = \frac{bh^3}{12} = \frac{1 \frac{15}{32} \left(\frac{11}{16}\right)^3}{12} = 0.0397 \text{ in}^4$$

$$\begin{aligned} I &= I_A + A_A d_A^2 + I_B + A_B d_B^2 \\ &= 0.01525 + 0.735 (0.469)^2 + 0.0397 + 1.008 (0.264)^2 \\ &= 0.686 \text{ in}^4 \end{aligned}$$

c. Calculation of the maximum fiber stress

It can be seen that the maximum bending moment occurs at both ends where $x = 0$. The most severe case is found over a bolt hole. Consider a pressure of 5000 psia exerted on the cell.

$$w = 5000 \times 1 \frac{15}{32} = 7350 \text{ lbs/in.}$$

$$M = \frac{wl^2}{12} = \frac{7350 \times 10^2}{12} = 61,200 \text{ in. lbs.}$$

$$f = -\frac{Mc}{I} = -\frac{61,200 \times 0.955}{0.686} = -85,400 \text{ lbs/in}^2$$

This is the maximum fiber stress in the uniformly loaded beam at its upper surface or the inside surface of the equilibrium cell. The lower surface has a maximum stress at

the end and is in compression.

$$f = - \frac{61,200 \times (- 0.855)}{0.686} = 76,400 \text{ lbs/in}^2$$

It can be seen that both these values are below the yield stress for 316 stainless steel. A factor of safety was introduced by making the bolt holes for a running fit such that the bolts undergo compression. The face plates were also designed to absorb part of the above stresses. The inside surface of the equilibrium cell body was brought to a very high polish.

The cell was first pressure tested with mercury to a pressure of 5000 lbs/in² and then with methane to the same pressure. Both tests were conducted for 24 hours and no drop in pressure was observed at any time.

It should be noted that the above calculations are approximations only and are not to be taken as a rigorous solution for the determination of the stresses in the equilibrium cell.

2. Pressure Measurement and Control

A Ruska mercury displacement pump with a capacity of 250 cc and rated at 10,000 lbs/in² was used. The pump was equipped with a mercury reservoir, as shown in Figure 8 and could be isolated from the system thereby effecting a greater capacity.

When mercury is used in the presence of water and hydrogen sulfide a chemical reaction occurs yielding a black precipitate of mercuric sulfide. This is extremely undesirable because the mercuric sulfide hampers visual observation of the hydrate and the occurrence of the reaction changes the composition of the system. A good confining fluid should have

- a. a property of being unreactive to the components of the system
- b. a low solubility of the gaseous components of the system
- c. a specific gravity greater than one
- d. a low viscosity

Selleck, Carmichael and Sage(20) in a study of the hydrogen sulfide-water system used a liquid known as fluorolube(6), a polymerized tetrafluoromethane having a viscosity of 150 centipoise at 100°F. Hydrogen sulfide was reported to be insoluble in this material. Fluorolube was completely unreactive to all the component gases but nevertheless methane was found to be highly soluble in this material. Furthermore, at low temperatures, fluorolube became very viscous and difficult to handle.

In view of the time required to find materials with the suitable properties it was decided to use mercury and to minimize the mercuric sulfide problem. A 150 cc bomb denoted as C in Figure 8 was placed between the equilibrium cell and

the mercury displacement pump. After bomb C was filled with water it was isolated from the system with valves 10 and 13. When the gaseous mixture was finally prepared, water could be introduced into the equilibrium cell without any mercury being present. Diffusion of hydrogen sulfide inevitably occurs but the mercuric sulfide reaction takes place in bomb C and the equilibrium cell does not become contaminated. Changes in composition attributable to the mercuric sulfide reaction were negligible.

Pressure was measured using two Heise Bourdon tube gauges rated at 5000 lbs/in² and 1500 lbs/in². Both gauges were calibrated with a Ruska dead weight tester to accuracies of 3 lbs/in² for the 5000 lbs/in² gauge and 0.5 lb/in² for the 1500 lb/in² gauge.

3. Temperature Measurement and Control

A bath with a capacity of fifteen gallons of varsol and equipped with two immersion heaters and refrigeration coils was used to control the temperature of the equilibrium cell. The immersion heaters were rated one at 500 watts and the other at 1000 watts, while the refrigerator was rated at one ton of refrigeration. Freon-12 was used as the refrigerant and the minimum attainable temperature was -4°F. A centrifugal pump immersed in the varsol and powered by a small electric motor was used for circulation through the lucite jacket surrounding the equilibrium cell.

Temperature was measured using an iron-constantan thermocouple inserted into the side of the equilibrium cell. Calibration of the thermocouple is shown in Table 6 of the appendix. A Leeds and Northrup Model 8686 millivolt potentiometer was used for determining the emf. generated.

4. Materials and Auxiliary Equipment

Auxiliary cells A and B, connected as shown in Figure 8, were used for the preparation of a gas mixture of a given composition. Cell A was rated at 1000 lbs/in², cell B was rated at 3000 lbs/in² and both were constructed of 316 stainless steel. The gaseous components were allowed to enter these cells followed by injection into the main equilibrium cell. Using this type of assembly, very small quantities of any gas could be displaced into the equilibrium cell.

All tubing, valves, and fittings were 1/8-inch Autoclave capable of withstanding 15,000 lbs/in².

Two shields of 1/4-inch mild steel plate to fit on both sides of the equilibrium cell were constructed as a precautionary measure in the event of a failure. In one of these a slot was cut at the level of the equilibrium cell and a mirror was mounted to allow indirect observation. A trouble light was used to illuminate the contents of the cell. The hydrate could easily be observed with the use of a cathetometer.

Evacuation of the system was accomplished with a small vacuum pump capable of drawing to a pressure of 0.05 mm

of mercury.

Methane and hydrogen sulfide gases were obtained from the Matheson Company of Canada and carbon dioxide was supplied by the Liquid Carbonic Company. All three gases were certified to be 99.5 percent chemically pure.

B. Experimental Procedure

The experimental procedure involved three steps as follows:

1. Preparation of a vapor mixture of a desired composition.
2. Measurement of the pressures at which the hydrate forms over a range of temperatures for each composition.
3. Analysis of the vapor phase at each equilibrium condition.

1. The Preparation of a Vapor Mixture

Since mixtures of hydrogen sulfide and carbon dioxide in the presence of water are extremely corrosive even to 316 stainless steel, it was essential that no water be present while the mixture was being prepared. Prior to injecting the first component, the equilibrium cell was brought to 100°F and compressed nitrogen was passed through it. The cell and the rest of the system were then evacuated for 24 hours.

Hydrogen sulfide, having the lowest vapor pressure of the three components, was injected first. Carbon dioxide

was the next component and the contents were allowed to mix by diffusion for 24 hours. The cell contents were then analyzed and more carbon dioxide was added. This iterative procedure continued until the correct ratio of carbon dioxide to hydrogen sulfide was attained. Methane was introduced into the system in exactly the same fashion as was carbon dioxide until a mixture of the correct composition was obtained.

2. Hydrate Formation

Water was injected into the cell by displacement with mercury in bomb C shown in Figure 8. Since both hydrogen sulfide and carbon dioxide are highly soluble in water, only a small quantity was used in order to minimize any change in composition.

The temperature was lowered to approximately ten degrees below the expected hydrate formation point and agitation was commenced to initiate crystal growth. As the temperature was increased, the point where the crystals began to melt was observed and maintained until the hydrate had completely melted. By tilting the equilibrium cell slightly to wet the glass window, the microscopic seed crystals could be seen as very small specks by using a cathetometer. Lowering the temperature by 0.5°F allowed the crystals to grow very slowly into very well defined and striking hexagonal patterns. Very carefully and slowly the temperature was raised until the newly formed crystals melted. This condition of

temperature and pressure was recorded as that for hydrate formation. The gas phase was then sampled.

3. Vapor Phase Analysis

Analyses were done using a Burrell Corporation Model K-2 gas chromatograph equipped with an eight-foot long hair-pin glass column. The column packing was 20 percent ansul ether on firebrick.

Peak height was considered to be a function of sample volume, helium flow rate, and temperature. The volumes of several samplers as well as the volume of the manifold in which they fit were measured by displacement with mercury. For each component in every sampler a peak height was measured and a curve of volume versus peak height was plotted. Mixtures of known composition were made up and analyzed using the smallest sampler. When the ratio of peak height in the mixture to the pure component peak height was taken, the value was always high for all components. The error in each component appeared to be independent of the relative amounts of the other two components. Normalization was a completely unsatisfactory means of correction for this error. It was decided to analyze many gas mixtures of known composition in order to determine the deviations over a range of compositions, especially in the region of interest. Correction curves of true percentage versus the ratio of peak height in the mixture to peak height of the pure component were plotted. These, along with the calibration curves are presented in the Appendix. Analyses were reproducible to within ± 0.5 percent.

V. EXPERIMENTAL RESULTS

A. The Methane-Carbon Dioxide-Water System

Hydrate equilibria for the methane-carbon dioxide-water system have been studied by Unruh and Katz(22) and have been reproduced in part by this work in order to develop a satisfactory experimental technique. A vapor mixture of carbon dioxide and methane was prepared and the three phase equilibria determined. Phase equilibria in the three phase region (HL_1V) for a ternary system has an additional degree of freedom over that of the binary system. This means that in ternary systems the hydrate will melt over a range of temperatures while in the binary system any condition in which the three phases exist is an equilibrium condition. For this reason, the experimental technique was developed using a ternary system. The data are presented in Table 1 of the appendix and are compared to the data of Unruh and Katz in Figure 9.

B. The Methane-Carbon Dioxide-Hydrogen Sulfide-Water System

A vapor phase mixture of 71 percent methane, 22.8 percent carbon dioxide and 5.2 percent hydrogen sulfide was prepared and its hydrate equilibria were determined as shown

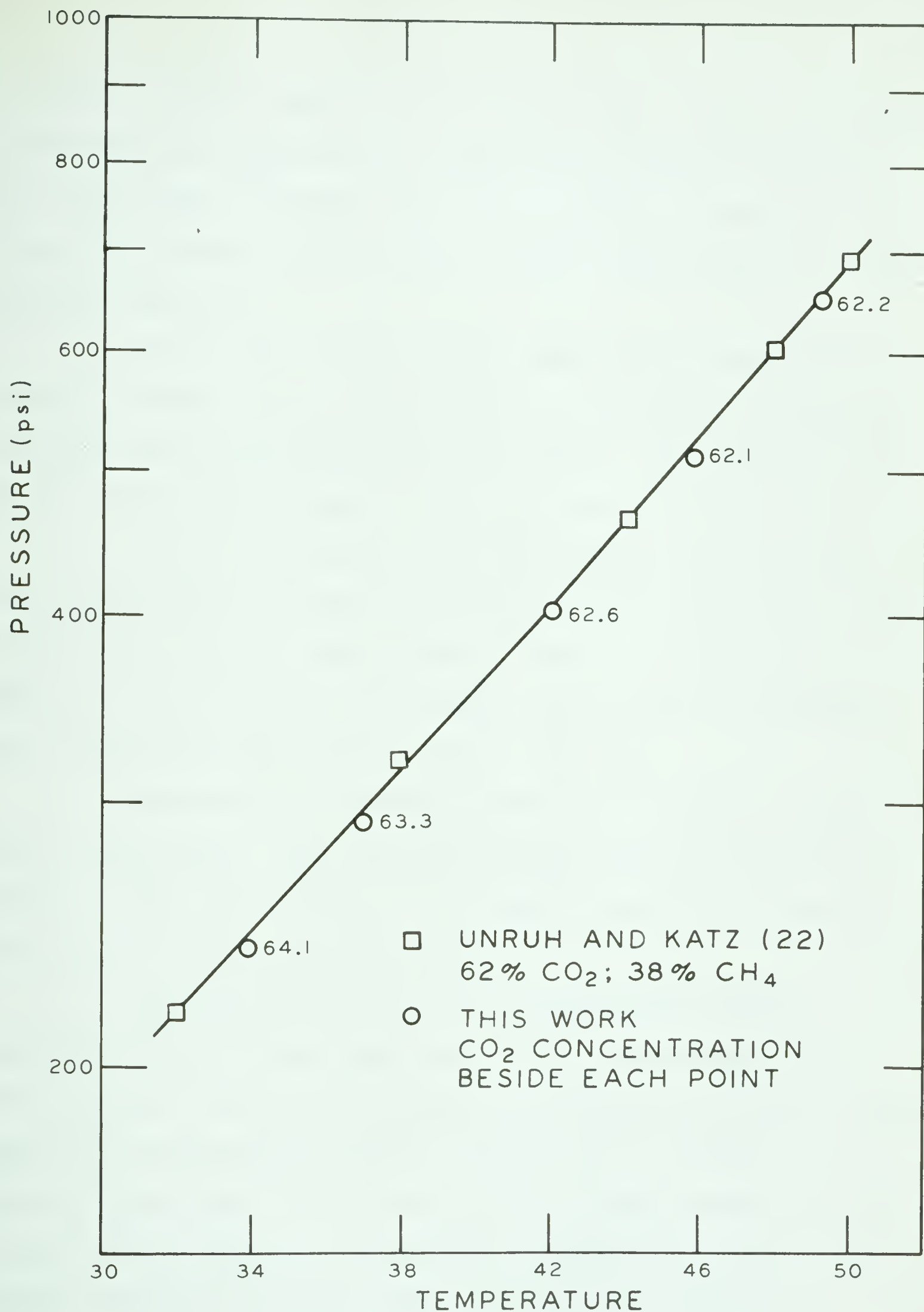


FIG.9 HYDRATE EQUILIBRIA (HL,V) FOR A TERNARY OF 62% CO₂ 38% CH₄ SYSTEM

in Table 2 of the appendix and in Figure 10. As was previously mentioned, the compositions changed due to water solubility. The curve shown in Figure 10 is of a constant composition of 72 percent methane, 22.3 percent carbon dioxide and 5.7 percent hydrogen sulfide.

Similarly, another vapor phase mixture having 72 percent methane but 12 percent carbon dioxide and 16 percent hydrogen sulfide was prepared and studied. The data for this mixture are shown in Table 3 and are plotted in Figure 10.

Using equilibrium ratios as defined by Carson and Katz, an attempt was made to calculate initial hydrate forming conditions for these two mixtures. The calculated data are shown in Tables 2 and 3 with sample calculations and percent deviations presented further in the appendix.

Similarly, two mixtures both at 82 percent methane were investigated. The results of these studies are given in Tables 4 and 5 and Figure 11. As before, equilibrium ratios were used to calculate these curves.

Figures 12 and 13 show the isothermal hydrate equilibria data of Unruh and Katz(22) for the methane-carbon dioxide-water system and of Noaker and Katz(13) for the methane-hydrogen sulfide-water system, respectively. Initial hydrate forming conditions for a mixture of 72 percent methane and 28 percent carbon dioxide are plotted on Figure 10 from the isothermal hydrate equilibria data of Figure 13. Similarly, initial hydrate forming conditions for a mixture of 72 percent

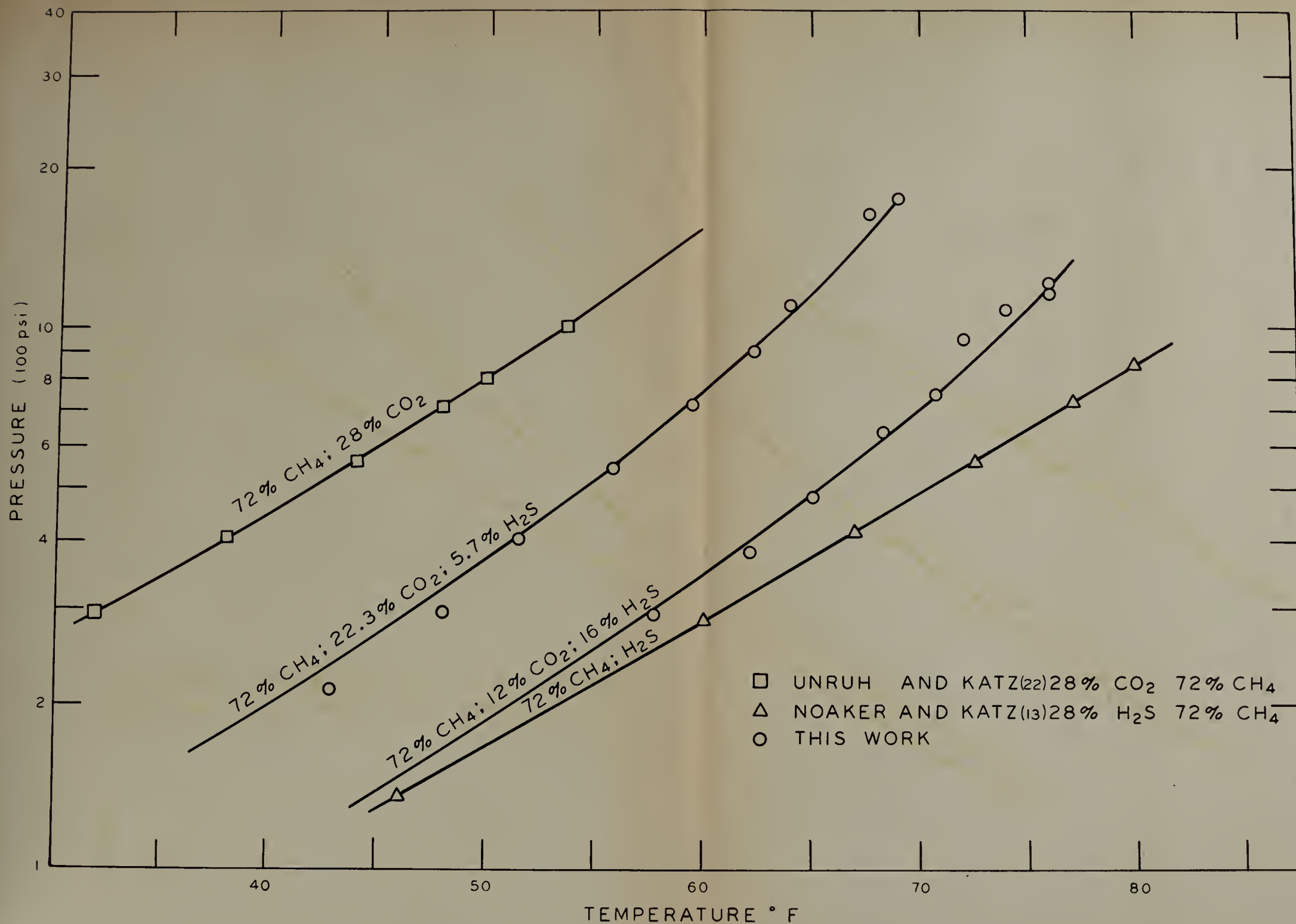


FIG.10 HYDRATE EQUILIBRIA FOR SYSTEMS OF 72% CH₄ WITH MAKE UP OF CO₂ AND H₂S

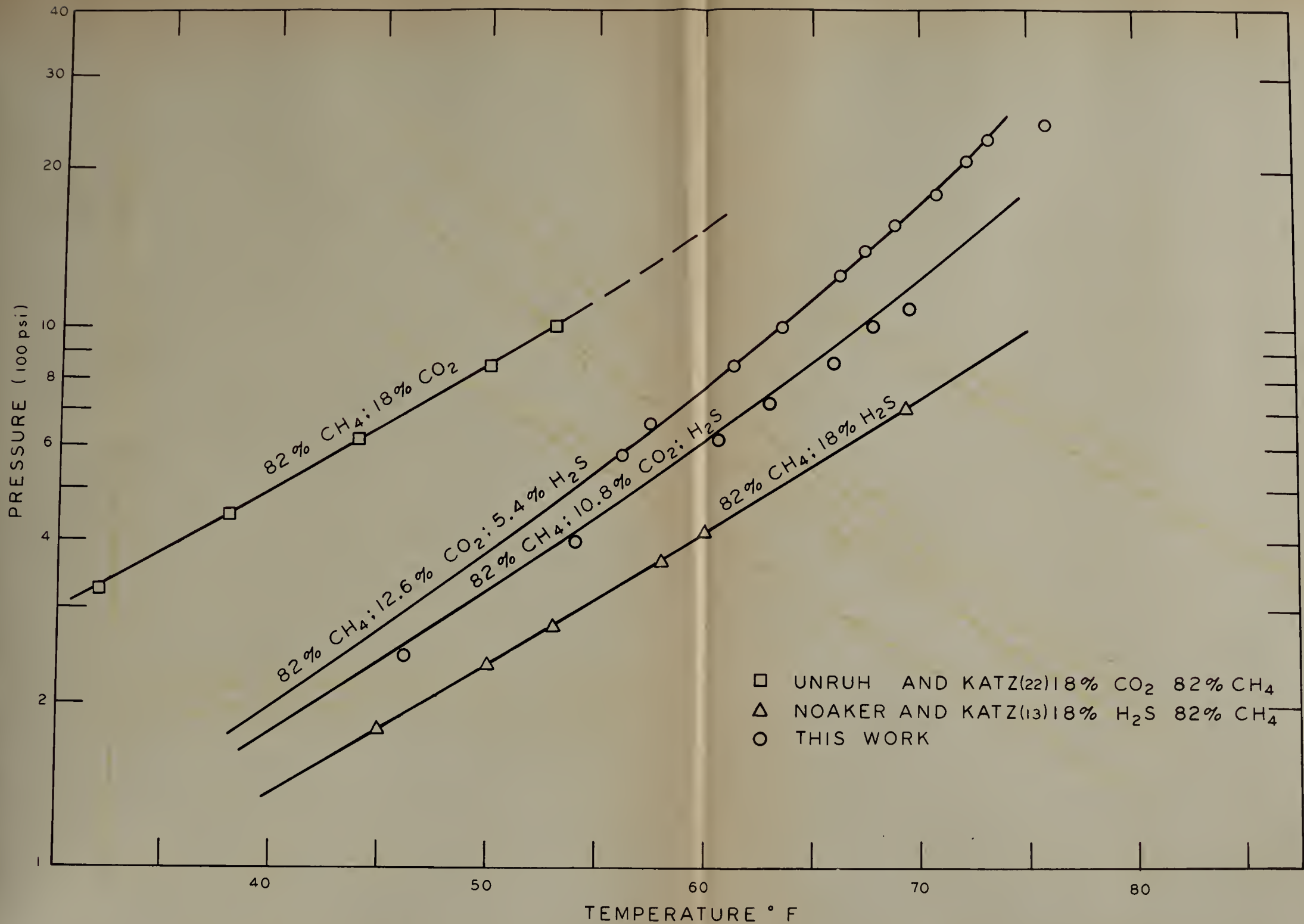


FIG. II HYDRATE EQUILIBRIA FOR SYSTEMS OF 82% CH₄ WITH MAKE UP OF CO₂ AND H₂S

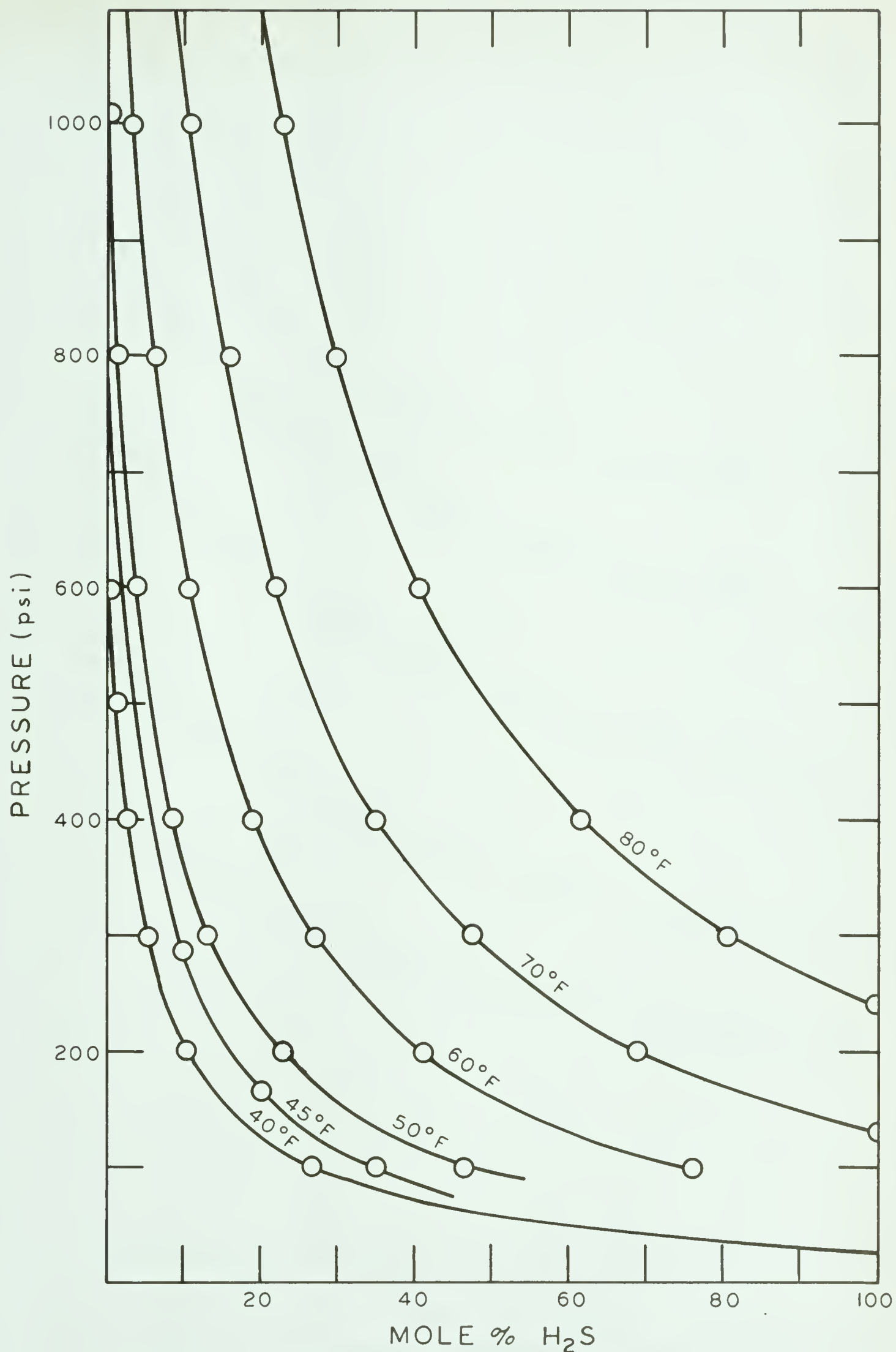


FIG.12 ISOTHERMAL HYDRATE EQUILIBRIA (HL₁V)
FOR THE TERNARY SYSTEM OF CH₄-H₂S-H₂O
BY NOAKER AND KATZ (13)

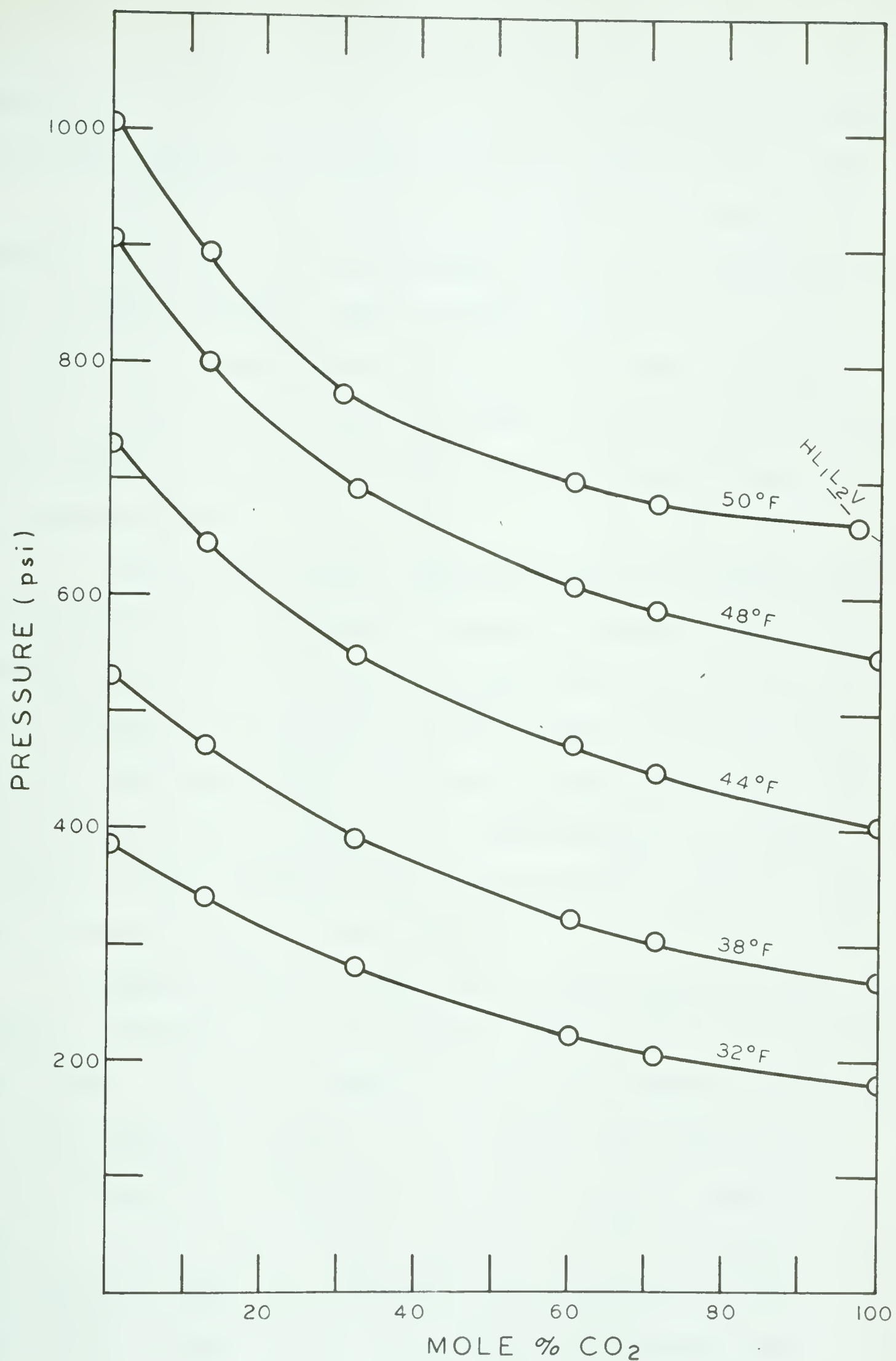


FIG.13 ISOTHERMAL HYDRATE EQUILIBRIA (HL₁V)
FOR THE TERNARY SYSTEM CH₄-CO₂-H₂O
BY UNRUH AND KATZ (22)

methane and 28 percent hydrogen sulfide are plotted on Figure 10 from the isothermal hydrate equilibria data of Figure 14.

Using Figures 12 and 13 in a similar fashion, hydrate equilibria for the systems of 82 percent methane, 18 percent carbon dioxide, and 82 percent methane, 18 percent hydrogen sulfide are plotted on Figure 11. Note that all curves on Figure 10 represent systems containing 72 percent methane while all curves on Figure 11 represent systems of 82 percent methane.

Isothermal hydrate equilibria data for systems of 72 percent methane and varying ratios of carbon dioxide to hydrogen sulfide are directly plotted from Figure 10 as shown in Figure 14. Similarly, for systems of 82 percent methane, isothermal hydrate equilibria data are plotted from Figure 11 as shown in Figure 15. The abscissae for Figures 14 and 15 are on a methane free basis because for both, the methane concentration is constant.

Figures 16 and 17 may best be described with an example. Consider a hydrate forming system with the following composition: 75 percent methane, 20 percent carbon dioxide and 5 percent hydrogen sulfide. On a methane free basis this becomes 80 percent carbon dioxide and 20 percent hydrogen sulfide. If the equilibrium pressure at 45°F is desired, one can obtain one point at a methane concentration of 72 percent from Figure 14 and one point at a methane concentration of

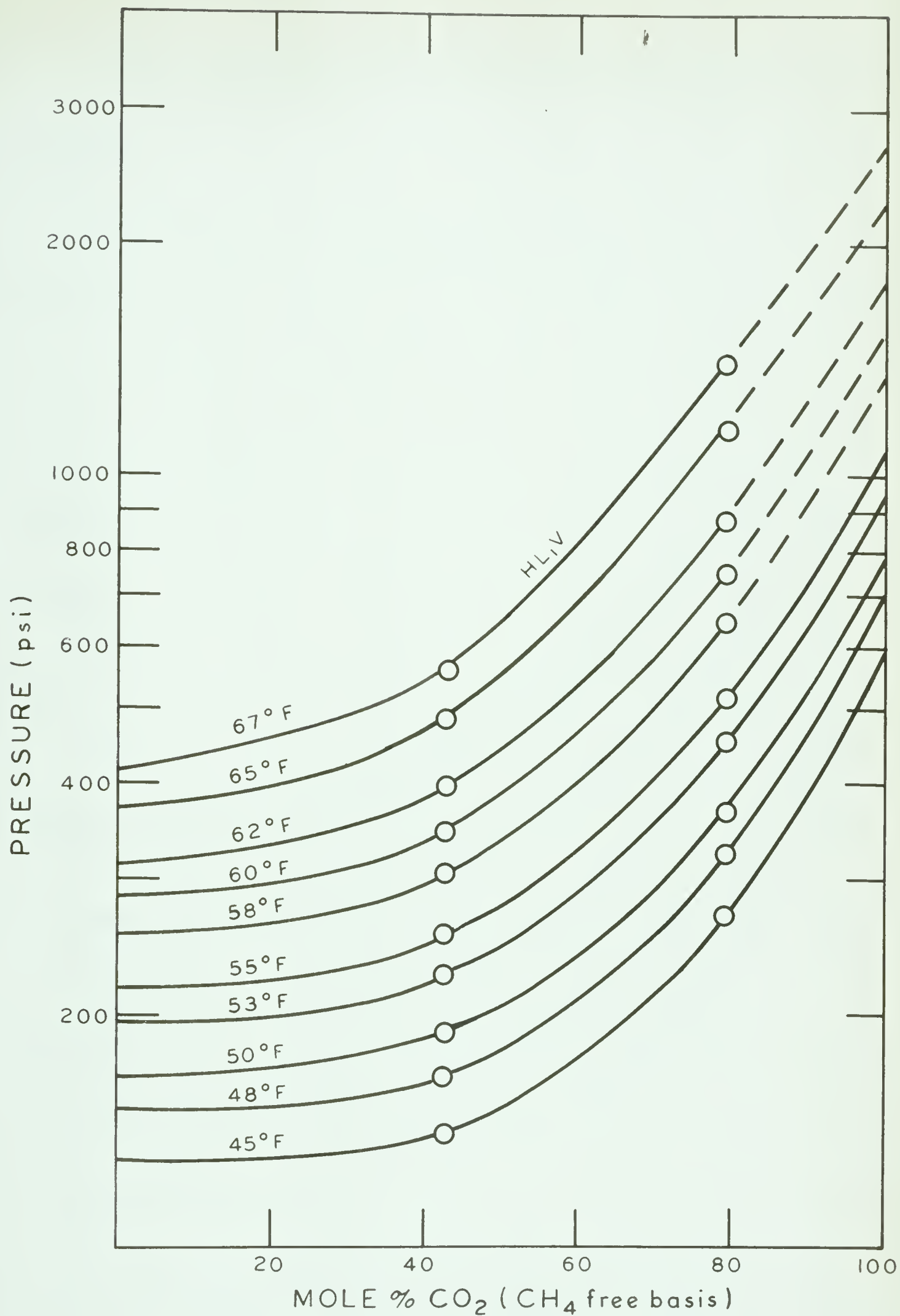


FIG.14 ISOTHERMAL HYDRATE EQUILIBRIA (HL_IV)
FOR QUATERNARY SYSTEMS OF 72% CH₄
AND MAKE UP OF CO₂ AND H₂S

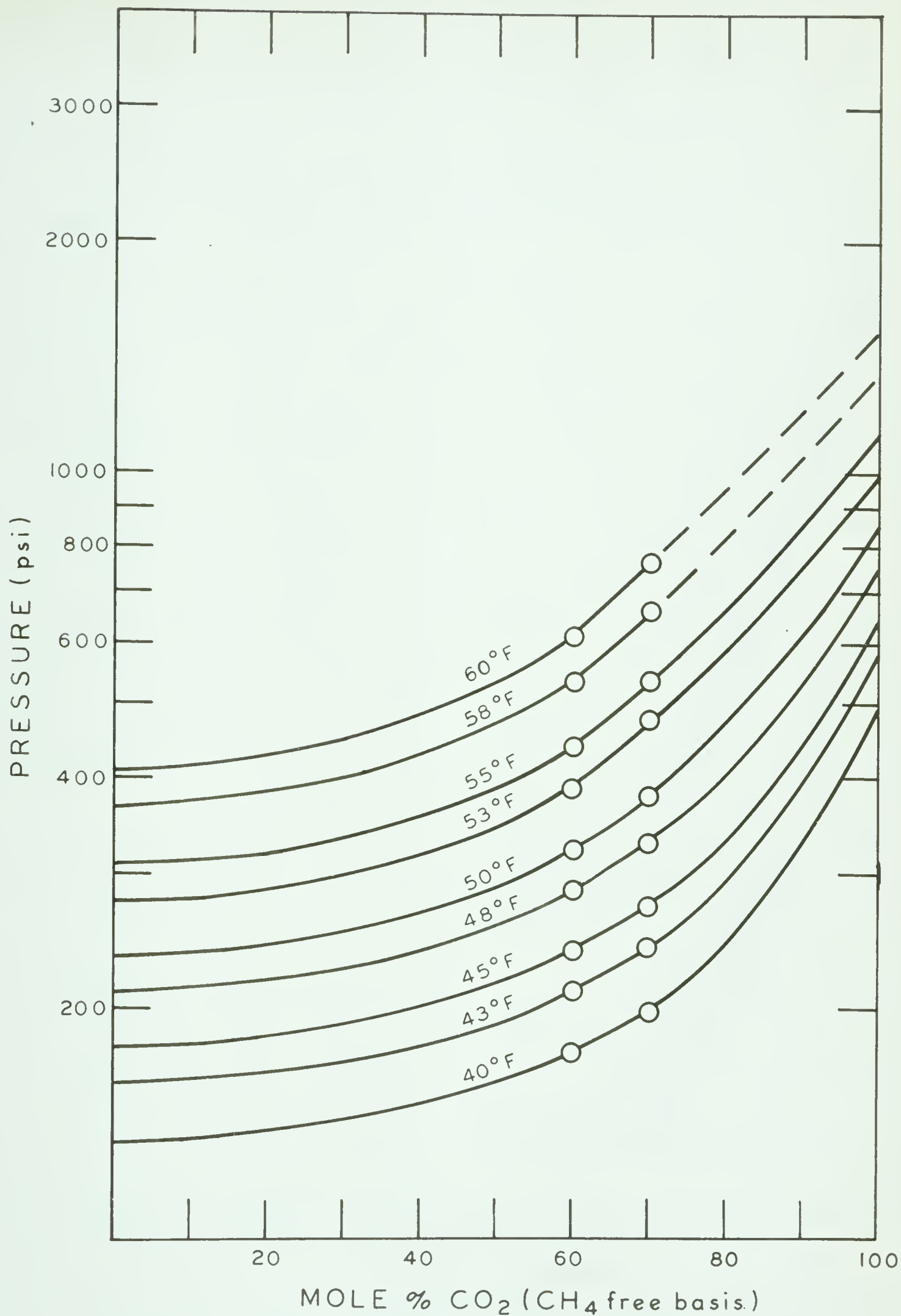


FIG.15 ISOTHERMAL HYDRATE EQUILIBRIA (HL₁V)
FOR QUATERNARY SYSTEMS OF 82% CH₄
AND MAKE UP OF CO₂ AND H₂S

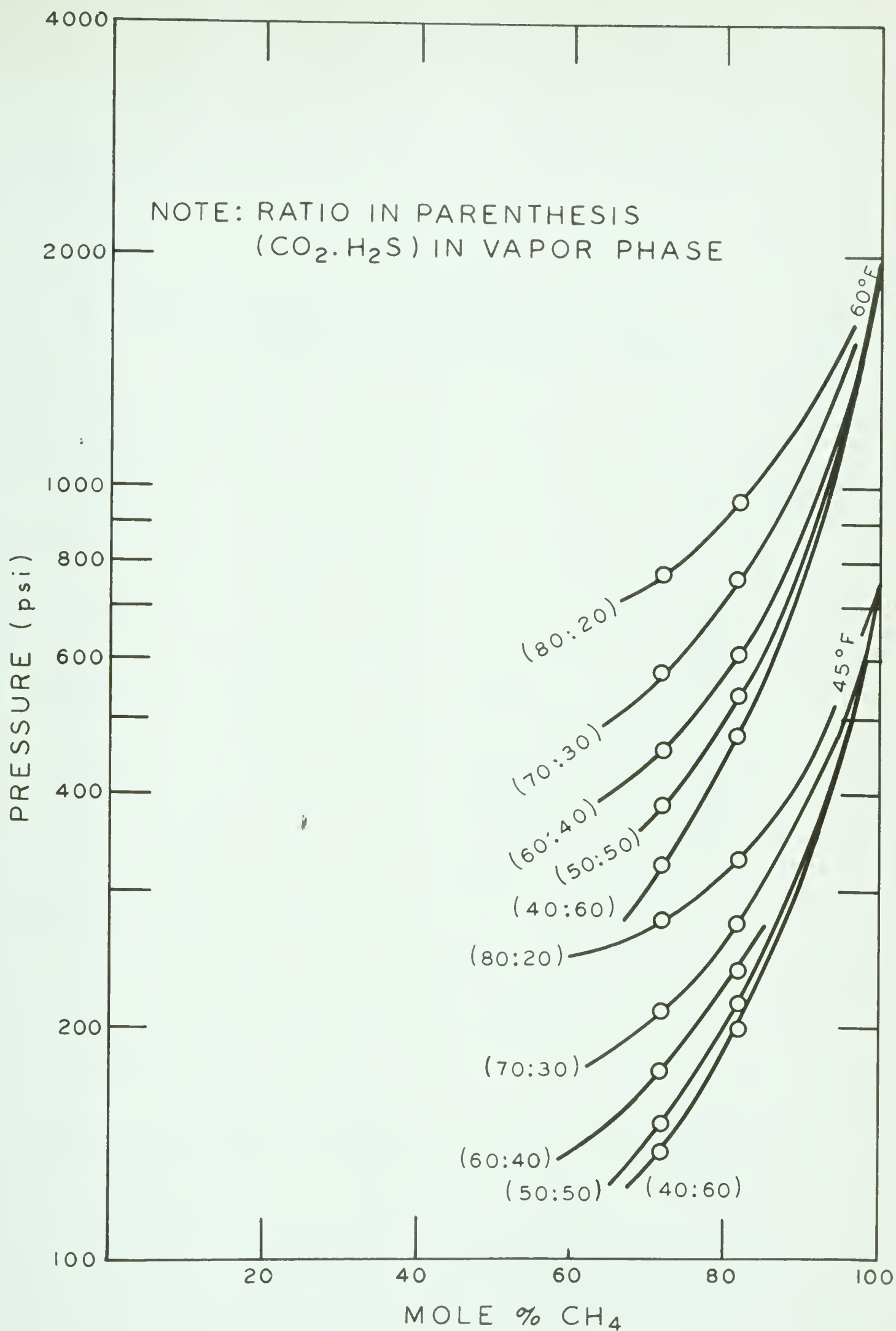


FIG.16 ISOTHERMAL HYDRATE EQUILIBRIA (HL₁V)
FOR THE QUATERNARY SYSTEM OF
CH₄-CO₂-H₂S-H₂O (DATA FROM FIG.14 AND 15
AT 45°F AND 60°F

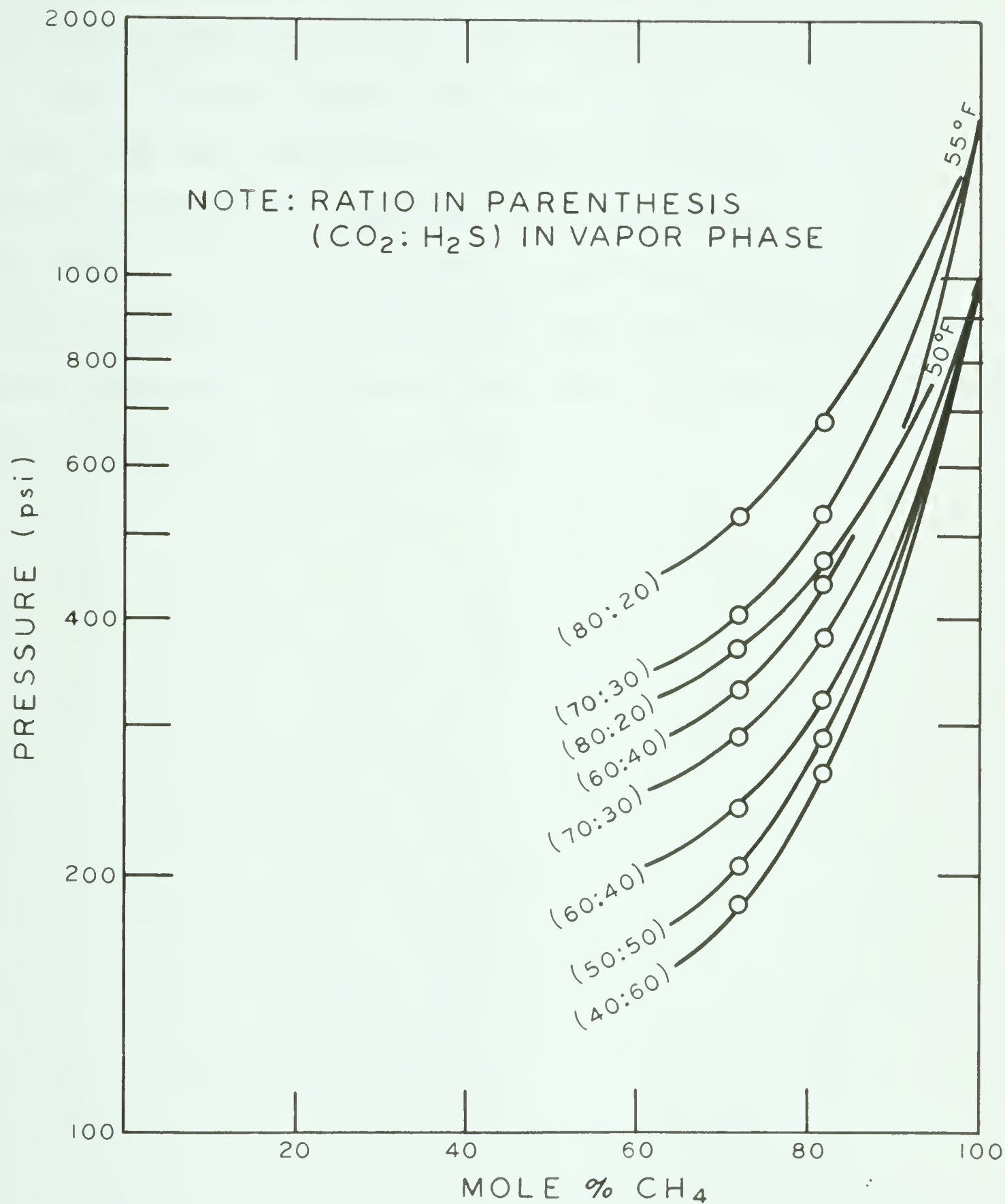


FIG. 17 ISOTHERMAL HYDRATE EQUILIBRIA (HL₁V) FOR THE QUATERNARY SYSTEM OF CH₄-CO₂-H₂S-H₂O (DATA FROM FIG. 14 AND 15 AT 50°F AND 55°F)

82 percent from Figure 16. A third point is obtained from the hydrate equilibria of the binary methane-water system. If a curve is drawn through the three points it can readily be seen that the equilibrium pressure is 290 lbs/in² abs. Prediction of hydrate equilibria may be achieved up to temperatures of 60°F and methane concentrations down to 65 percent. Systems of high methane concentration were chosen because they were of interest and would not form a solute-rich liquid (L₂) phase.

VI. DISCUSSION

A. Measurement of Variables

Pressures could be determined to accuracies of ± 0.5 lbs/in² with the 1500 lbs/in² gauge and ± 3 lbs/in² with the 5000 lbs/in² gauge. Temperature measurements were accurate $\pm 0.5^\circ\text{F}$. Throughout the course of this investigation frequent checks were made on the calibration curves and correction curves used in the chromatographic analysis. It was observed that peak height slowly decreased over an extended period of time but that the correction curves remained unchanged. Analyses are thought to be within an error of 0.5 percent.

In view of the fact that visual observation is required for determining initial hydrate forming conditions it follows that personal errors may become significant. Saito and Kobayashi(18) use a technique where visual observation of melting is not necessary. Using a time programmed temperature system, they could control the rate at which the temperature was raised very accurately while making continuous observations of temperature and pressure. As the temperature was raised the pressure would rise very rapidly until the hydrate had completely dissociated. Beyond this point the slope would decrease to the normal pressure temperature behavior of the gas phase. Such behavior is illustrated with Figure 18. The point at which the discontinuity occurs is considered to be the initial hydrate forming condition.

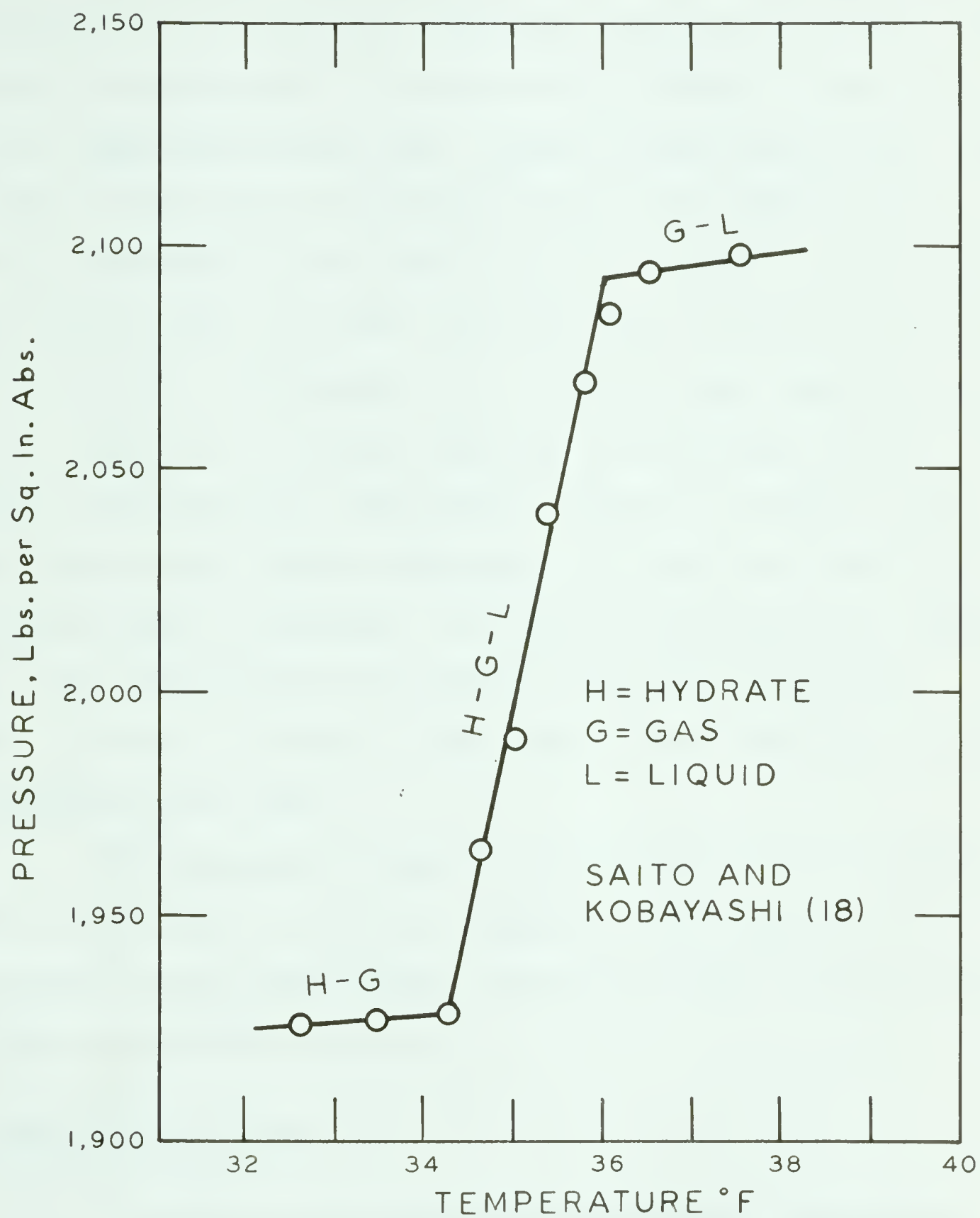


FIG.18 TYPICAL DECOMPOSITION CURVE FOR ARGON NITROGEN HYDRATE

An attempt was made to apply this method in this investigation. Without the sensitive temperature control used by Saito and Kobayashi, it became very difficult to manually control temperature such that a sharp discontinuity could be observed at the point of disappearance of the hydrate phase. Upon extrapolation of the two curves to a point of intersection it was found that this point deviated from the data of Unruh and Katz by 5°F. Throughout this attempt visual observations were also made and it became obvious that non-equilibrium behavior was occurring. The hydrate tended to remain in the liquid-water phase under conditions of temperature and pressure which make it unstable. In view of the available equipment it was decided that the visual approach was superior since, as shown in Figure 9, the data of Unruh and Katz could be reproduced very well.

This attempt to apply a new method was not completely without value for it served to emphasize the importance of there being only a few hydrate crystals present at the point of incipient hydrate formation.

B. Equilibrium Ratios

A comparison was made between hydrate equilibrium predicted using equilibrium ratios of Carson and Katz and that determined experimentally. Deviations are shown in Table 7 of the appendix. The concept of equilibrium ratios is not entirely

satisfactory, for the prediction of initial hydrate forming conditions. Robinson and Jhaveri(8) account for this in the following way:

"It is apparent ... that the hydrate composition depends on the nature of the molecular constants and on the characteristics of the lattice cavities. Hence, equilibrium ratios for Structure I systems would not be expected to agree with Structure II systems even for similar components."

They go further to state:

"Theoretical considerations show that the concentration of gases in a hydrate depends on the partial pressure of the gas in the gas phase, on constants related to each of the species of molecules present in the gas phase and on the nature of the crystal lattice itself. For this reason, calculations of initial hydrate forming conditions in multi-component systems which are based on equilibrium ratios obtained on specific systems must be regarded as approximations only."

As in vapor-liquid equilibria, the equilibrium ratio is not a function of temperature and pressure alone, but must also be considered a function of composition. The failure of calculated and experimental hydrate forming conditions to agree is further confirmation of this fact. Composition of the hydrate is a function of the structure in which it exists. It follows that equilibrium ratios for carbon dioxide and hydrogen sulfide determined for systems in which these components are present with methane are not completely correct since these systems hydrate in Structure I and the methane propane system hydrates in Structure II. Equilibrium ratios in their present form would certainly not

be expected to predict accurately hydrate forming conditions of the quaternary system studied in this work.

CONCLUSIONS

The study of hydrates of the methane-carbon dioxide-hydrogen sulfide system has contributed to the available data on hydrate forming systems. Hydrogen sulfide has been shown to exert a considerable influence on initial hydrate forming conditions even when it is present in low concentrations.

By various graphical operations it has been shown that the quaternary system can be represented in a relatively simple way. By this means hydrate equilibria for this system may be predicted for methane concentrations from 65 to 100 percent with no restriction on the ratio of hydrogen sulfide to carbon dioxide.

It has further been shown that the use of equilibrium ratios in their present form is not a satisfactory means for the prediction of hydrate equilibria of multicomponent systems.

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A P P E N D I X

TABLE 1

Experimental Hydrate Equilibria (HL₁V)

Data for the CH₄-CO₂-H₂O System

Temp. °F	Pres. lbs/in ²	Composition of Gas Phase	
		% CO ₂	% CH ₄
49.2	652	62.2	37.8
45.7	517	62.1	37.9
42.1	405	62.6	37.4
36.9	293	63.3	36.7
33.9	240	64.1	35.9

TABLE 2

Calculated and Experimental Hydrate Equilibria (HLV) for a

Vapor Phase Mixture of Approximately 72% CH₄; 22.3% CO₂; 5.7% H₂S

Temp. °F	Calculated Pres. lbs/in ² abs.	Temp. °F	Pres. lbs/in ² abs.	Experimental		
				% CH ₄	% CO ₂	% H ₂ S
35.3	200	42.8	214	68.6	24.9	6.5
42.0	300	48.0	295	69.9	24.1	6.0
47.0	400	51.5	402	70.5	23.5	6.0
50.5	500	55.8	543	71.5	22.8	5.7
53.3	600	59.5	715	72.5	22.0	5.5
57.0	800	62.3	897	72.5	22.0	5.5
59.5	1000	64.0	1095	72.5	22.0	5.5
		67.7	1628	72.0	22.3	5.7
		69.0	1742	72.3	22.2	5.5

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TABLE 3

Calculated and Experimental Hydrate Equilibria (HL₁V) for a
 Vapor Phase Mixture of Approximately 72% CH₄; 12% CO₂; 16% H₂S

Temp. °F	Calculated Pres. lbs/in ² abs.	Temp. °F	Pres. lbs/in ² abs.	Experimental Vapor Phase Composition		
				% CH ₄	% CO ₂	% H ₂ S
32.0	100	54.0	184			
44.5	200	57.7	293	69.9	12.7	17.4
51.4	300	62.2	384	70.0	12.3	16.7
56.5	400	65.0	483	72.0	12.0	16.0
		68.3	637	72.0	12.0	16.0
		70.7	743	72.0	12.0	16.0
		72.0	942	71.1	11.9	17.0
		74.0	1071	70.8	12.1	17.1
		76.0	1219	72.5	11.9	15.6
		76.0	1161	68.8	13.6	17.6

1 58 1

TABLE 4

Calculated and Experimental Hydrate Equilibria (HLIV) for a

Vapor Phase Mixture of Approximately 82.0% CH₄; 10.8% CO₂; 7.2% H₂S

Temp. °F	Calculated Pres. lbs/in ² abs.	Temp. °F	Pres. lbs/in ² abs.	Experimental		
				% CH ₄	% CO ₂	% H ₂ S
40.2	250	35.2	102	78.9	13.6	7.5
43.2	300	51.8	276	81.0	11.8	7.2
48.0	400	54.0	401	81.0	11.8	7.2
52.5	500	60.7	617	80.0	12.0	8.0
55.5	600	63.0	722	80.0	12.0	8.0
		66.0	862	80.0	12.0	8.0
		67.8	1013	81.6	11.1	7.3
		69.5	1092	83.9	9.4	6.7
		75.8	2416	85.0	8.7	6.3

1 59 1

TABLE 5

Calculated and Experimental Hydrate Equilibria (HLV) for a

Vapor Phase Mixture of Approximately 82.0% CH₄; 12.6% CO₂; 5.4% H₂S

Temp. °F	Calculated		Temp. °F	Pres. lbs/in ² abs.	Experimental		
	Temp. °F	Pres. lbs/in ² abs.			Pres. lbs/in ² abs.	%CH ₄	% CO ₂ % H ₂ S
34.0		200	46.2	243	78.5	13.9	7.6
41.0		300	48.8	330	80.3	13.0	6.7
46.0		400	56.2	516	81.0	13.0	6.0
52.3		600	57.5	661	82.0	12.6	5.4
56.2		800	61.3	854	82.0	12.6	5.4
59.0		1000	63.7	998	82.0	12.6	5.4
			66.3	1255	82.0	12.5	5.5
			67.5	1397	82.0	12.6	5.4
			68.8	1565	82.0	12.6	5.6
			70.8	1790	82.5	12.1	5.4
			72.3	2042	82.0	12.6	5.4
			73.8	2278	82.0	12.6	5.4

1
0
1

TABLE 6

Thermocouple Calibration

<u>Temp.</u>	<u>TC Error</u>
32.0 °F	- 0.1 °F
77.5 °F	- 0.2 °F
207.9 °F	- 0.3 °F

Sample Calculations

Prediction of conditions for hydrate formation.

<u>Component</u>	<u>Mole Fraction in Gas Phase y</u>	<u>K for Component at 40.5 °F 250 psia</u>	<u>y/k = z</u>
CH ₄	0.820	1.98	0.414
CO ₂	0.108	1.45	0.075
H ₂ S	0.072	0.145	0.496
	<hr/>		<hr/>
	1.000		0.985

The assumed temperature of 40.5 °F is too high try 40.0 °F

CH ₄	0.820	1.97	0.415
CO ₂	0.108	1.40	0.077
H ₂ S	0.072	0.140	0.515
	<hr/>		<hr/>
	1.000		1.007

The assumed temperature of 40.0 °F is too low.

Interpolation between this and the previous result gives a temperature of 40.2 °F.

TABLE 7

Comparison of Calculated and Experimental
Conditions for Hydrate Formation

Pressure	Calculated Temp.	Experimental Temp.	Percent Deviation
200	34.0	40.2	15.4
300	41.0	46.4	11.6
400	46.0	50.7	9.3
600	52.3	56.6	7.6
800	56.2	60.6	7.3
1000	59.0	63.6	7.2

Gas Composition

82.0% CH₄

12.6% CO₂

5.4% H₂S

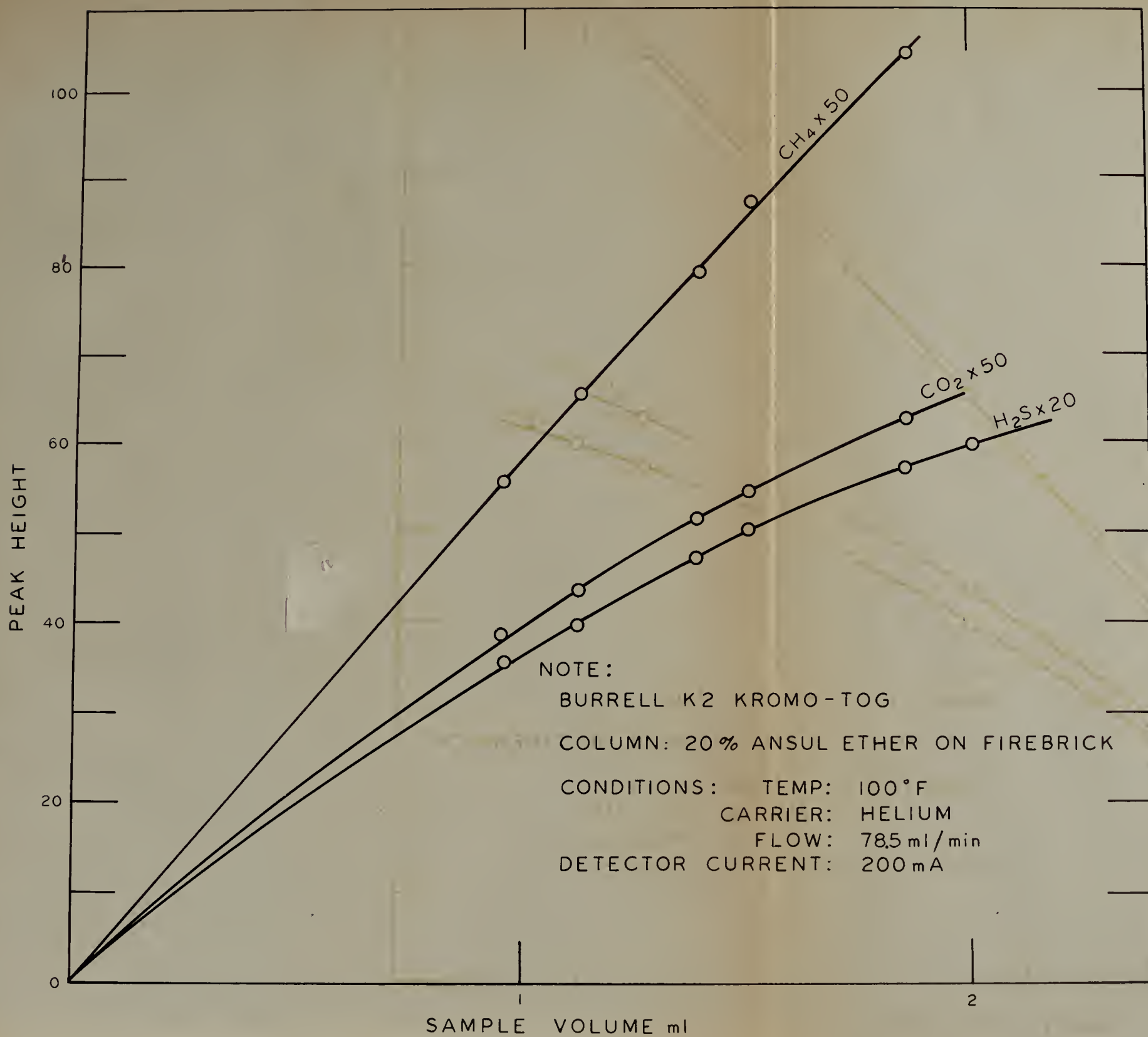


FIG.19 CHROMATOGRAPH CALIBRATION CURVES FOR CH₄, CO₂, H₂S



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